HEAT

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PREFACE.

It was with considerable hesitation that I sanctioned the Publishers' proposal to print a very large number of copies of the first edition of this work. Some of my reasons will be found in the former Preface, reprinted below:—especially those depending on the fact that the work was written, in occasional intervals of comparative leisure, during several very busy years.

It is, therefore, with proportionate pleasure that I now find I can reissue it with a very moderate amount of alteration:—the only serious error discovered (besides other pretty obvious typographical ones) being the unaccountable omission of some necessary words in the important quotation from Clerk-Maxwell given in § 442.

But Teachers, who have used the book, have kindly pointed out to me passages in which they or their pupils had found unexpected difficulty:—and I have endeavoured to make these passages more clear.

I have also rewritten the section which deals with the isothermals of gases from the point of view of the kinetic theory. Here temperature, of which so much was said in the former Preface, reappears in an even more formidable guise than before.

P. G. TAIT.

College, Edinburgh,
November 2nd, 1891.

PREFACE TO THE FIRST EDITION.

This work originated in an article which I contributed in 1876 to the *Handbook to the Loan Collection of Scientific Apparatus* (at South Kensington). As that article was based upon the system of teaching the subject of Heat which, after many years' experience, I have found best adapted to the wants of intelligent students taking up the subject for the first time, Mr. Macmillan asked me to develop it in the form of an elementary treatise. In 1876—7 a large portion of the work was written; the greater part of which was put in type, and had the advantage of Clerk-Maxwell's valuable criticism. Some of the earlier chapters were utilised when I had to give at short notice an evening discourse at the *British Association* Meeting in 1876.

Pressing work of a very different character, such as the examination of the *Challenger* Thermometers, interfered from time to time with my writing by occupying most of my leisure. I have at last managed to finish the book, as nearly as possible on the lines laid down at starting; but it cannot, under the circumstances, be expected to have the unity which it might have secured by being continuously written.

It may be asked—Why publish another text-book on a subject which is already thoroughly treated in the excellent (and strictly scientific) works of Clerk-Maxwell and Balfour Stewart? The only answer, and it may be a sufficient one, is:—Clerk-Maxwell's work is on the *Theory of Heat*, and is specially fitted for the Study; that of Stewart is rather for the Physical Laboratory; so that there still remains an opening for a work suited to the Lecture Room. By that expression I mean a work suitable for students who, without any intention of entering on a scientific career, whether theoretical or experimental, are yet desirous of knowing accurately the more prominent facts and theories of modern science to such an extent as to give them an intelligent interest in physical phenomena.

In addition to what is stated in the text (§ 11) as to the special arrangement and division of the subject in the present work, it may be well to say a few words here as to the way in which the important subjects of temperature, and especially of absolute temperature, have been treated.

Temperature is first introduced as a mere condition determining which of two bodies in contact shall part with heat to the other (§ 6). In this sense it is compared to the *pressure* of the air in a receiver, the air itself being the analogue of heat (§ 52). When two such receivers are made to communicate with one another, air passes from that in which the pressure is greater to that in which it is less. And this is altogether independent of the relative quantities of air in the two receivers.

In § 57 it is pointed out that there is an *absolute* method of defining temperature, which must therefore be the sole scientific method. But it is also stated that, in experimental work, few quantities are directly measured in terms of the strictly scientific units in which they are ultimately to be expressed. In § 60 the reader is told that what is wanted, to prepare him for the absolute measurement of temperature, is "something which shall be at once easy to comprehend and easy to reproduce, and which shall afterwards require only very slight modifications to reduce it to the rigorous scale."

Thus (§ 61) a *temporary* centigrade scale is defined by means of mixtures of ice-cold water and boiling water. And this is *stated* to "accord so closely with the absolute scale, that careful experiment is required even to show that it does not exactly coincide with it."

In terms of temperatures thus defined, the questions of Expansibility, Latent and Specific Heats, &c., are explained from the experimental point of view.

But, before these are taken up, the first rapid *résumé* of the whole subject introduces Carnot's Cycles, and his principle of Reversibility, with Thomson's application of them to the absolute measurement of temperature. It is pointed out (§ 95) that Carnot's results still leave a certain option in the formal definition of absolute temperature, and that Thomson found it possible so to frame his definition (which is given at this stage) as to make a very close agreement between the new scale and that of an ordinary air-thermometer. Thus, the use of air-thermometer temperatures is justified by their close approximation to absolute temperatures, as well as by their comparative simplicity and convenience, for the chapters which follow; and they are thenceforth employed until (by means of the Indicator Diagram) it has been fully pointed out what is the scientific importance of absolute temperature. It is then shown, in § 405, how to compare absolute temperature with that given by the air-thermometer.

All *à priori* notions as to strict logical order, however valuable, and in fact necessary, in a formal treatise, must be set aside in an elementary work, if they be found in practice to impede rather than assist the progress of the average student. And it is solely on this ground that the above system of exposition has been adopted in the present work.

He who expects to find this work, elementary as it is, everywhere easy reading, will be deservedly disappointed. No branch of science is free from real and great difficulties, even in its elements. Any one who thinks otherwise has either not read at all, or has confined his reading to pseudo-science.

The reader, who wishes to know more of the general science of Energy than was admissible into the present work, will find a connected historical sketch of it in my little book on *Thermodynamics*. There he will also find more of the purely analytical development of the subject, specially from W. Thomson's point of view.

P. G. TAIT.

COLLEGE, EDINBURGH,
December 1*st*, 1883.

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CHAPTER I.

FUNDAMENTAL PRINCIPLES.

1. In dealing with any branch of physical science it is absolutely necessary to keep well in view the fundamental and all-important principle that

Nothing can be learned as to the physical world save by observation and experiment, or by mathematical deductions from data so obtained.

On such a text volumes might be written; but they are unnecessary, for the student of physical science will feel at each successive stage of his progress more and more profound conviction of its truth. He must receive it, at starting, as the unanimous conclusion of all who have in a legitimate manner made true physical science the subject of their study; and, as he gradually gains knowledge by this—*the only*—method, he will see more and more clearly the absolute impotence of all so-called metaphysics, or *a priori* reasoning, to help him to a single step in advance.

2. Man has been left entirely to himself as regards the acquirement of physical knowledge. But he has been gifted with various *senses* (without which he could not even know

that the physical world exists) and with *reason* to enable him to control and understand their indications.

Reason, unaided by the senses, is totally helpless in such matters. The indications given by the senses, unless interpreted by reason, are in general utterly unmeaning. But when reason and the senses work harmoniously together they open to us an absolutely illimitable prospect of mysteries to be explored. This is the test of true science—there is no resting-place—each real advance discloses so much that is new and easily accessible, that the investigator has but scant time to co-ordinate and consolidate his knowledge before he has additional materials poured into his store.

3. To sight, without reason, the universe appears to be filled with light—except, of course, in places surrounded by opaque bodies.

Reason, controlling the indications of sense, shows us that the sensation of sight is our own property; and that what we understand by brightness, &c., does not exist outside our minds. It shows us also that the sensation of colour is purely subjective, the only differences possible between different so-called rays of light outside the eye being merely in the extent, form, and rapidity of the vibrations of the luminiferous medium.

To hearing, without reason, the air of a busy town seems to be filled with sounds. Reason, interpreting the indications of sense, tells us that if we could *see* the particles of air we should observe among them (superposed upon their rapid motions among one another) simply a comparatively slow agitation of the nature of alternate compressions and dilatations. And our classification of sounds as to loudness, pitch, and quality, is merely the subjective correlative of what in the air-particles is objectively the amount of compression, the rapidity of its alternations, and the greater or less complexity of the alternating motion.

A blow from a stick or a stone produces pain and a bruise; but the motion of the stick or stone before it reached the body is as different from the sensation produced by the blow as is the alternate compression and dilatation of the air from the sensation of sound, or the ethereal wave-motion from the sensation of light.

Hence to speak of what we ordinarily mean by light, or sound, as existing outside ourselves, is as absurd as to speak of a swiftly-moving stick or stone as pain. But no inconvenience is occasioned if we announce the intention to use the terms light and sound for the objective phenomena, and to speak of their subjective effects as "luminous impressions" or "noise," as the case may be. In this sense there is outside us energy of motion of every kind, but in the mind mere corresponding impressions of brightness and colour, noise or harmony, pain, &c. &c.

4. It would seem therefore that we must be extremely cautious in our own interpretation of the immediate evidence of our senses as to heat. And the very first instance that occurs to us fully justifies this caution.

Touch, in succession, various objects on the table. A paper-weight, especially if it be metallic, is usually cold to the touch; books, paper, and especially a woollen table-cover, comparatively warm. Test them, however, by means of a *thermometer*, not by the sense of touch, and in all probability you will find little or no difference in what we call their *temperatures*. In fact, as we shall presently see, any number of bodies of any kind shut up in an enclosure (within which there is no fire or other source of heat) all tend to acquire ultimately the same temperature. Why then do some feel cold, others warm, to the touch?

The reason is simply this—the sense of touch does *not* inform us directly of temperature, but of *the rate at which our finger gains or loses heat.* As a rule, bodies in a room are colder than the hand, and heat always tends to pass from a warmer to a colder body. Of a number of bodies, all equally colder than the hand, that one will seem coldest to the touch which is able *most rapidly* to convey away heat from the hand. The question therefore is one of *conduction of heat.* And to assure ourselves that it is so, reverse the process: *let us,* in fact, *try an experiment,* though an exceedingly simple one; for the essence of experiment is to modify the circumstances of a physical phenomenon so as to increase its value as a test. Put the paper-weight, the books, and the woollen table-cloth into an oven, and raise them all to one and the same temperature, considerably above that of the hand. The woollen cloth will still be comparatively cool to the touch, while the metal paper-weight may be much too hot to hold. The order of these bodies, as to warm and cold in the popular sense, is in fact reversed; and this is so, because the hand is now *receiving* heat from all the various bodies experimented on, and it receives most rapidly from those bodies which in their previous condition were capable of abstracting heat most rapidly. However it may be in the moral world, in the physical universe the giving and taking powers of one and the same body are strictly correlative and equal.

5. Thus the direct indications of sense are in general utterly misleading as to the relative temperatures of different bodies.

In a baker's or a sculptor's oven, at temperatures far above the boiling-point of water (on one occasion even 320° F.), so high indeed that a beef-steak was cooked in thirteen minutes, Tillet in France, and Blagden and Chantrey in

England, remained for nearly an hour in comparative comfort. But, though their clothes gave them no great inconvenience, they could not hold a metallic pencil-case without being severely burned.

On the other hand, great care has to be taken to cover with hemp, or wool, or other badly conducting substance, every piece of metal which has to be handled in the intense cold to which an Arctic expedition is subjected; for contact with very cold metal produces sores almost undistinguishable from burns, though due to a directly opposite cause. Both of these phenomena, however, ultimately depend on the comparative facility with which heat is conducted by metals.

6. Even from the instance just given, the reader cannot fail to see that there is a profound distinction between heat and temperature. Heat, whatever it may be, is SOMETHING which can be transferred from one portion of matter to another; the consideration of temperatures is virtually that of the mere CONDITIONS which determine whether or not there shall be a transfer of heat, and in which direction the transfer is to take place.

In fact, we may without risk of misleading the student tell him, even at the beginning of his work, that from one point of view the quantity of heat in a body bears a very close analogy to the water-power stored up in a cistern or reservoir, while the temperature of the body is as closely analogous to the elevation of the cistern. He must notice, however, that water-power does *not* depend upon mere quantity of water: to be capable of driving a mill the water must have "head," or elevation.

But, in another and quite different sense, heat in a body is analogous to the water, not to the water-power. Heat tends to pass from a hotter to a colder body, just as water tends to flow from a cistern at a higher to another at a lower level. Thus heat in a hot body is in this property analogous to (or at least behaves like) water at a high level, and *vice versâ.*

Two such connected and yet different analogies can be safely presented to the student at an early stage; for they will certainly help his conceptions, and their difference will prevent his being in any way misled by either.

7. For all that, as will presently be seen, *heat—though not material—has objective existence in as complete a sense as matter has.*

This may appear, at first sight, paradoxical; but we must remember that so-called paradoxes are merely facts as yet unexplained, and therefore still apparently inconsistent with others already understood in their full significance.

When we say that matter has objective existence, we mean that it is something which exists altogether independently of the senses and brain-processes by which alone we are informed of its presence. An exact, or adequate conception of it, if it could be formed, would probably be something very different from any conception which our senses will ever enable us to form; but the object of all pure physical science is to endeavour to grasp more and more perfectly the nature and laws of the external world, by using the imperfect means which are at our command—reason acting as interpreter as well as judge; while the senses are merely the witnesses,—who may be more or less untrustworthy and incompetent, but are nevertheless of inconceivable value to us, because they are our only available ones.

8. Without further discussion we may state once for all that our conviction of the objective reality of matter is based mainly upon the fact, *discovered solely by experiment*, that we

cannot in the slightest degree alter its quantity. We cannot destroy, nor can we produce, even the smallest portion of matter. But reason requires us to be consistent in our logic; and thus, if we find anything else in the physical world whose quantity we cannot alter, we are bound to admit it to have objective reality as truly as matter has, however strongly our senses may predispose us against the concession. Heat, therefore, as well as Light, Sound, Electric Currents, &c., though not forms of matter, must be looked upon as being as real as matter, simply because they have been found to be forms of *Energy* (Chap III. below), which in all its constant mutations satisfies the test which we adopt as conclusive of the reality of matter.

But the student must here be again most carefully warned to distinguish between heat and the mere sensation of warmth; just as he distinguishes between the energy of motion of a cudgel and the pain produced by the blow. The one is the *thing* to be measured, the other is only the more or less imperfect reading or indication given by the instrument with which we attempt to measure it in terms of some one of its effects.

9. There is one other point which must be insisted on as a necessary preliminary to all physical inquiries, to wit, the condition under which alone it is possible that physical science can exist. We may enunciate it as follows:—

Under the same physical conditions the same physical results will always be produced, irrespective altogether of time or place.

It requires no comment whatever, if the terms employed be fully understood and be interpreted in the strictest sense. It is, in fact, merely the assertion (based entirely on observation and experiment) of the existence of definite and unchanging laws to which all physical processes are found to be subject.

CHAPTER II.

INTRODUCTORY.

10. UNTIL all physical science is reduced to the deduction of the innumerable mathematical consequences of a few known and simple laws, it will be impossible completely to avoid some confusion and repetition, whatever be the arrangement of its various parts which we adopt in bringing them before a beginner.

When we confine ourselves to one definite branch of the subject, all of whose fundamental laws can be distinctly formulated, there need be no such confusion. Here in fact the mathematician has it all in his own hands. He is the skilled artificer with his plan and his trowel, and the hodmen have handed up to him all the requisite bricks and mortar. This has long been known and recognised as a fact, but it has not often been put so neatly as in the following extract:—

"That which is properly called Physical Science is the knowledge of relations between natural phenomena and their physical antecedents, as necessary sequences of cause and effect; these relations being investigated by the aid of mathematics—that is, by a method in which processes of reasoning, on all questions that can be brought under the categories of *quantity* and of *space-conditions*, are rendered perfectly exact, and simplified and made capable of general application to a degree almost inconceivable by the uninitiated, through the use of conventional symbols. There is no admission for any but a mathematician into this school of philosophy. But there is a lower department of natural science, most valuable as a precursor and auxiliary, which we may call Scientific Phenomenology; the office of which is to observe and classify phenomena, and by induction to infer the laws that govern them. As, however, it is unable to determine these laws to be necessary results of the action of physical forces, they remain merely empirical until the higher science interprets them. But the inferior and auxiliary science has of late assumed a position to which it is by no means entitled. It gives itself airs, as if it were the mistress instead of the handmaid, and often conceals its own incapacity and want of scientific purity by high-sounding language as to the mysteries of nature. It may even complain of true science, the knowledge of causes, as merely mechanical. It will endue matter with mysterious qualities and occult powers, and imagines that it discerns in the physical atom 'the promise and potency of all terrestrial life.'" *

Thus all who have even a slight acquaintance with the subject know that the laws of motion, and the law of gravitation, contain absolutely all of *Physical Astronomy*, in the sense in which that term is commonly employed :—viz., the investigation of the motions and mutual perturbations of a number of masses (usually treated as mere points, or at least as rigid bodies) forming any system whatever of sun, planets, and satellites.

But, as soon as physical science points out that we *must*

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* *Church Quarterly Review*, April 1876, p. 149.

take account of the plasticity and elasticity of each mass of such a system, the amount and distribution of liquid on its surface, possibly of magnetic and other actions between them, and the resistance due to the medium in which they move; the simplicity of the data of the mathematical problem is gone; and physical astronomy, except in its grander outlines, becomes as much confused as any other branch of science.

So it is with the Dynamics of Solid and Fluid bodies:—so long as we are content to view solids as perfectly smooth and rigid, and fluids as incompressible and frictionless, the difficulties of Dynamics, though often enormously great, are entirely mathematical, it falls naturally into quite distinct and separate heads, and the classification of its various problems is comparatively simple. Introduce ideas of strain, and fluid friction, with consequent development of heat, and the confusion due to imperfect or impossible classification comes in at once. Each problem, instead of being treated by itself, has to borrow, sometimes over and over again, from others; and the only fully satisfactory and uncomplicated mode of attacking such a subject (were it conceivable) would be to *work it all out at once.*

11. Hence, in dealing with the general subject of heat we shall find it quite impossible to lay down definite lines of demarcation. Divide it as we choose, each part will be found to require for its development something borrowed from another.

All that we can do under these conditions (the existence of which simply means that we do not yet know all about heat in the same sense as we may be said to know the laws of motion and of gravitation) is to make our classification confessedly somewhat indefinite, and freely to assume throughout, when needed, results of other parts of our subject which we have not yet discussed. The advantages of this method, at least in my own experience, have been found much to outweigh its obvious but as yet inevitable disadvantages. But, to reduce the latter as far as possible, I shall first go over the whole subject briefly, so as to point out its main features and their mutual relations; *explaining* some of the more important things, though not giving their experimental proof; and thus the student will be from the outset fairly prepared to take up in turn each of our divisions of the subject with as much detail as is consistent with the dimensions of an elementary treatise. And another advantage will be gained, inasmuch as such a rapid and general glance at the whole subject will admit of a number of useful and even important digressions which would seriously impair the consistency of the more detailed and definite part of the work.

12. The classification I have found convenient is as follows:—

1. Nature of Heat.
2. Effects of Heat.
3. Measurement of Heat and of Temperature.
4. Sources of Heat.
5. Transference of Heat.
6. Transformations of Heat.

As already pointed out, there is no hard and fast line drawn between any two of these heads, in fact the explanations of many even among ordinary phenomena belong in part to more than one of them.

It is well, however, to remark that there is a very intimate connection between the three heads (1), (4), and (6) above, which contain among them the chief recent advances of the *Dynamical Theory of Heat*, or *Thermodynamics*, as it is commonly called. Hence (1) will be more fully developed than the other heads in our first rapid *résumé* of the whole subject, while its farther development will be wholly merged in that of (4) and (6), which may then profitably be studied together. Again (3) depends, at least in all its ordinary practical forms, on some application or other of one of the group (2). (5) stands to a great extent by itself, but naturally divides itself into three perfectly distinct processes, all of which are of great scientific as well as practical importance.

CHAPTER III.

DIGRESSION ON FORCE AND ENERGY.

13. We must now take up briefly and in order these divisions of our subject; but before we can do so intelligibly, a digression into the elements of *Dynamics* is absolutely essential. This involves, in fact, the citation and explanation of a passage in Newton's *Principia* which, till very lately, seems to have altogether escaped the notice of scientific men. The reader will find that the consideration of this passage, especially when he sees it rendered into the terms used in modern science, will greatly facilitate his farther progress with regard to the nature of heat.

Newton's *Third Law of Motion* is to the effect that—

"*To every action there is always an equal and contrary reaction; or, the mutual actions of any two bodies are always equal and oppositely directed.*"

This law Newton first shows to hold for ordinary pressures, tensions, attractions, &c., that is, for what we commonly call *forces* exerted on one another by two bodies; also for impacts, or impulses, which are merely the time-integrals of forces.

But he proceeds to point out that the same law is true in another and much higher sense. He says:—

"*If the activity of an agent be measured by the product of its* *force into its velocity; and if, similarly, the counter-activity of the resistance be measured by the velocities of its several parts into their several forces, whether these arise from friction, cohesion, weight, or acceleration;—activity and counter-activity, in all combinations of machines, will be equal and opposite.*"

The actions and reactions which are here stated to be equal and opposite are no longer simple forces, but the *products* of forces into their velocities; *i.e.* they are what are now called *Rates of doing Work;* the time-rate of increase, or the increase per second, of a very tangible and real SOMETHING: for the measurement of which Watt introduced the practical unit of a *horse-power*, the rate at which an agent works when it lifts 33,000 pounds one foot high per minute, against the earth's attraction.

14. Now let the reader think of the difference between raising a hundredweight and endeavouring to raise a ton. With a moderate exertion he can raise the hundredweight a few feet, *and in its descent it might be employed to drive machinery, or to do some other species of work.* Let him tug as he pleases at the ton, he will not be able to lift it; and therefore after all his exertion, it will not be capable of doing any work by descending again.

In both cases the first interpretation of Newton's *Third Law* has been verified. With whatever force he pulled either of the masses, that mass reacted with an equal force. But the second interpretation cannot be applied to the ton; *for it did not acquire any velocity*, it was not moved. Hence, as no work was spent upon it, it has not acquired the power of doing work. On the other hand, the hundredweight was moved, work was done upon it, and that work was stored up in it in its raised position, ready for use at any future time. Newton's statement implies that in this case the work spent in raising the hundredweight is stored up (without change of amount) in the mass when raised.

15. Thus it appears that *force* is a mere name; but that the *product of a force into the displacement of its point of application* has an objective existence. [Even those who are so metaphysical as not to see that the product of a *mere name* into a *displacement* can have objective existence, may perhaps see that the quotient of a horse-power by a velocity is not likely to be more than a mere name.] In fact, modern science shows us that force is merely a convenient term employed for the present (very usefully) to shorten what would otherwise be cumbrous expressions; but it is not to be regarded as a *thing;* any more than the bank *rate of interest* is to be looked upon as a sum of money, or than the birth-rate of a country is to be looked upon as the actual group of children born in a year. And a very simple mathematical operation shows us that it is precisely the same thing to say—

The horse-power of an agent, or the amount of work done by an agent in each second, is the product of the force into the average velocity of the agent:

and to say—

*Force is the rate at which an agent does work per unit of length.**

16. In the special illustration of Newton's words which we have just given, the resistance was a *weight*, that of a hundredweight or of a ton. When the resistance was

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* In symbols—this is merely

$$\frac{dw}{dt} = fv = f\frac{dx}{dt}, \text{ the first statement,}$$

whence

$$\frac{dw}{dx} = f, \text{ the second.}$$

overcome, work was done, and it was stored up for use in the raised mass—in a form which could be made use of at any future time.

Following a hint given by Young, we now employ the term ENERGY to signify the power of doing work, in *whatever* that power may consist. The raised mass, then, we say, possesses in virtue of its elevation an amount of energy precisely equal to the work spent in raising it. This dormant, or passive, form, is called *Potential* Energy. Excellent instances of potential energy are supplied by water at a high level, or with a "head," as it is technically called, in virtue of which it can in its descent drive machinery;—by the wound-up "weights" of a clock, which in their descent keep it going for a week;—by gunpowder, the chemical affinities of whose constituents are called into play by a spark; &c. &c.

Another example of it is suggested by the word "Cohesion" employed in Newton's statement (§ 13), and which must be taken to include what are called molecular forces in general, such as for instance those upon which the elasticity of a solid depends.

When we draw a bow we do work, because the force exerted has a velocity; but the drawn bow (like the raised weight) has in potential energy the equivalent of the work so spent. That can in turn be expended upon the arrow; and *what then?*

17. Turn again to Newton's words (§ 13) and we see that he speaks of one of the forms of resistance as arising from "*acceleration.*" In fact, the arrow, by its inertia, resists being set in motion; work has to be spent in propelling it:—but the moving arrow has that work in store in virtue of its motion. It appears from Newton's previous statements that the measure of the rate at which work is spent in producing

acceleration* is *the product of the momentum into the acceleration in the direction of motion*, and the energy produced is measured by *half the product of the mass into the square of the velocity produced in it.* This active form is called *Kinetic* Energy, and it is the double of this to which the term *Vis Viva* (erroneously translated Living Force) has been applied.

As instances of ordinary kinetic energy, or of mixed kinetic and potential energies, take the following:—A current of water capable of driving an undershot wheel; winds, which also are used for driving machinery; the energy of water-waves or of sound-waves; the radiant energy which comes to us from the sun, whether it affect our nerves of touch or of sight (and therefore be called radiant heat or light) or produce chemical decomposition, as of carbonic acid and water in the leaves of plants, or of silver-salts in photography (and be therefore called actinism); the energy of motion of the particles of a gas, upon which its pressure depends, &c. [When the motion is vibratory the energy is generally half potential, half kinetic.]

18. These explanations and definitions being premised, we can translate Newton's words (without alteration of their meaning) into the language of modern science, as follows:—

Work done on any system of bodies (in Newton's statement the parts of any machine) *has its equivalent in work done against friction, molecular forces, or gravity, if there be no acceleration; but if there be acceleration, part of the work is expended in overcoming the resistance to acceleration, and the*

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* Let $\dot{v}$ be the acceleration, in the direction of motion, of a mass M whose velocity is v. Then Newton's expression for the rate of spending work against the resistance to acceleration is $M\dot{v} . v$, or as above, $Mv . \dot{v}$, and the whole work spent in giving the velocity v to the mass M, originally at rest, is $\frac{1}{2} Mv^2$.

additional kinetic energy developed is equivalent to the work so spent.

But we have just seen that when work is spent against molecular forces, as in drawing a bow or winding up a spring, it is stored up as potential energy. Also it is stored up in a similar form when done against gravity, as in raising a weight.

Hence it appears that, according to Newton, whenever work is spent, it is stored up either as potential or as kinetic energy:—except possibly in the case of work done against friction, about whose fate he gives us no information. Thus Newton expressly tells us that (except possibly when there is friction) *energy is indestructible*—it is changed from one form to another, and so on, but never altered in quantity. To make this beautiful statement complete, all that is requisite is to know *what becomes of work done against friction.*

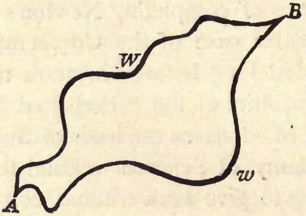
19. Here, of course, experiment is requisite. Newton, unfortunately, seems to have forgotten that savage men had long since been in the habit of making it whenever they wished to procure fire. The patient rubbing of two dry sticks together, or (still better) the drilling of a soft piece of wood with the slightly blunted point of a hard piece, is known to all tribes of savages as a means of setting both pieces of wood on fire. Here, then, heat is undoubtedly produced, *but it is produced by the expenditure of work.* In fact, work done against friction has its equivalent in the heat produced. This Newton failed to see, and thus his grand generalization was left, though on one point only, incomplete. The converse transformation, that of heat into work, dates back to the time of Hero at least. But the knowledge that a certain process will produce a certain result does not necessarily imply even a notion of the "why"; and Hero

as little imagined that in his Œolipile heat was *converted* into work, as do savages that work can be *converted* into heat.

Rumford and Davy, at the very end of last century, by totally different experimental processes, showed conclusively that the materiality of heat could not be maintained; and thus gave the means of completing Newton's statement.

20. One particular case of the Conservation of Energy had been formulated long before Newton's time, under the title of the Impossibility of the "Perpetual Motion." This was employed by Stevinus as the basis of Statics. In 1775 the French Academy of Sciences refused to consider any scheme pretending to give work without corresponding and equivalent expenditure. The multiplied experiments of some of the most ingenious men who have ever lived have been directed to obtaining the Perpetual Motion, and their absolute failure in every case may be taken as proof of the impossibility. One mode of reasoning from this acknowledged impossibility may be here explained by a particular instance, as it will be found very useful in some of the more theoretical parts of our subject.

We employ it to show that in all cases of natural laws, such as the laws of gravitation and of magnetic attraction, the work spent in moving a body through a certain course in one direction is exactly restored by letting it return to its first position, not merely by the original path but by any other; always on the supposition that friction is avoided. Suppose there could be two courses, from A to B, by the one of which more work would be spent on the mass than by the other. Let these amounts be W and w. If such were the case the Perpetual Motion could be produced. Apply frictionless constraint to guide the mass, so that in its ascent it shall travel along the course A w B, and in its descent, along B W A. From A to B the amount w of work is spent against the forces of the system—from B to A these forces refund the amount W. On the whole, after a complete cycle, the mass is restored to A with an amount W — w of energy additional to what it possessed at starting.



Every time the mass goes round the double course in the same direction it gains the difference between the larger quantity and the smaller one, and therefore at the end of each complete cycle, that amount may be drained off to turn some machine ;—to do useful work.

We here assume that the work spent in one course would be exactly recovered by letting the mass retrace its steps ; in other words, that the operation is *reversible*. This term will be fully discussed later.

In general, if there were one way of doing a thing at less cost than another, and if the more costly operation were reversible, it would be possible to get unlimited amounts of useful work from nothing.

We are now prepared to undertake the short general glance over our subject promised in § 11, according to the plan there laid down.

CHAPTER IV.

PRELIMINARY SKETCH OF THE SUBJECT.

21. **Nature of Heat.**—Heat, under the name of fire, which seems to have included everything either really or apparently of the nature of flame, such as sun and moon, stars, planets, and comets, lightning and Aurora, &c., as well as ordinary fire, was in old times regarded as one of the so-called *Four Elements*, of which, or of some of which, it was imagined that everything in the physical world was necessarily composed.

The tendency of early experimental science, which took its first great impulse, if not its absolute origin, from Gilbert of Colchester (*circa* 1570), was to regard heat, light, electricity, &c., as forms of matter—excessively subtle and refined—capable of freely pervading and combining with all ordinary gross matter. They were, in fact, classed as *Imponderables*, because a heated or electrified body, for instance, was not found to be increased in weight by the heat or electricity which it was supposed to have imbibed.

22. In this sense heat was supposed to be an excessively light species of matter, and was called *Caloric*, or, in certain of its manifestations (especially in some chemical processes), *Phlogiston* :—though, as has been recently shown,* the latter

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* Crum Brown, *Proc. R.S.E.*, 1870.

term was also used to describe certain forms of what we now call chemical potential energy. (The meaning of this term will be obvious from the statement above (§ 16) regarding the energy of gunpowder.)

The notion of the materiality of heat or caloric, in spite of experiments proving the contrary, and of several shrewd guesses* as to their true nature, was all but universally accepted and taught till about 1840. Then commenced that rapid revolution which has entirely altered the generally accepted views of heat, just as a few years previously the *Material* or *Corpuscular Theory of Light* may be said to have received its death-blow; or, as in somewhat more recent times, the so-called *Electric Fluids* have been banished from all British science except some portions of that spurious and worse than useless kind which is commonly called *popular*.

23. One by one the *Imponderables* have been displaced from their old and proud position in science; but they have all died hard, and among many of the continental schools of physicists, and especially of the German, the electric

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* "And tryall hath taught me that there are liquors, in which the bare admixture of milk, oyle, or other liquors—nay, or of cold water, will presently occasion a notable heat: and I sometimes imploy a *menstruum*, in which nothing but a little flesh being put, though no visible Ebullition ensue, there will in a few minuts be excited a Heat, intense enough to be troublesome to him that holds the Glasse. And yet it seems not necessary that this should be ascrib'd to a true fermentation, which may rather proceed from the perturb'd motion of the Corpuscles of the menstruum, which being by the adventitious liquor or other body put out of their wonted motion, and into an inordinate one, there is produced in the menstruum a brisk confus'd Agitation of the small parts that compose it; and in such an agitation (from what cause soever it proceeds), the nature of heat seems mainly to consist."—*Some Considerations touching the Usefulness of Experimental Naturall Philosophy*. By Robert Boyle. Part II., Section 1, p. 45. 1663.

fluids still retain (thanks to an exceedingly ingenious idea of W. Weber, quite as good in its way as Newton's *Fits of Easy Reflection and Transmission*) their position as, in a certain sense, forms of imponderable matter, acting on one another according to a very peculiar law, quite different from anything met with in other branches of physics. But even there the end must soon come, when this last trace of the imponderables shall be handed over for preservation in the museum of the scientific antiquary.

24. The experiments, which, as stated in § 22, first proved that heat is not matter, are due to Rumford and Davy, and date from 1798 and 1799 respectively.

The explanation of the heat produced by friction which was given by those who believed heat or caloric to be matter was simply this: The body in its solid state, or rather in its massive state, before you began to abrade filings from it, possessed, at any particular temperature, a certain quantity of heat. It had a certain *capacity* for heat, as it was called; in other words, it required so much heat to be mixed up with its particles in order to make the temperature of the whole that which was observed. But if you could make it more capacious—if you could give it greater capacity for heat—then it would hold more heat without becoming of a higher temperature. On the other hand, if by any process whatever you could diminish its capacity for heat, then, of course, it would become hotter in itself, and even give out heat to surrounding bodies; so that, according to the notion of the supporters of this theory, the production of heat by friction or abrasion is due to the fact that you make the capacity of a body for heat smaller by reducing it to powder. For of course, when its capacity for heat is thus made smaller, it must part with some of the heat it had at first; or if it retains it, it must necessarily show the effect of the heat more than it did before, and must therefore rise in temperature. Now this reasoning is, so far, perfectly philosophical, and we can say nothing against it as a mode of reasoning. But it involves the fallacious assumption that heat is matter, and therefore indestructible.

25. Next, see how well Rumford laid hold of that point, and how he proceeds by experiment to try if possible to satisfy his doubts about it. He says :—

> "If this were the case, then, according to the modern doctrines of latent heat, and of caloric, the *capacity for heat* of the parts of the metal so reduced to chips, ought not only to be changed, but the change undergone by them should be sufficiently great to account for *all* the heat produced."

Rumford found no difference, so far as his form of experiment enabled him to test them, between the capacities for heat of the abraded metal and of the metal before the abrasion had taken place: so that if this additional experiment had only been a satisfactory one :—and Rumford did not see how to make it thoroughly satisfactory :—the fact that heat is not matter would have been conclusively established in 1798. What Rumford really did want was a test to bring the abraded metal and the non-abraded metal, if possible, precisely to the same final state. He tried to do that by throwing them into water—equal masses of the metal in lumps and filings, each raised to the same high temperature, into equal quantities of water at the same lower temperature, to see whether they would produce different changes of temperature, each in its own vessel of water.

26. But then they were not in the same final state. The filings were not in the same state as the solid metal; they might have been very considerably compressed, or they might have been distorted in shape, and in virtue of these

they might have had a certain quantity of latent heat which Rumford could not discover by this process. The simplest legitimate process which we know of for completely answering this question, which was Rumford's sole difficulty, is a chemical process. Dissolve the lumps and an equal weight of the filings in equal quantities of an acid. At the end of the operation, of course, there can be no doubt that the chemical substances produced will be precisely the same, whether you begin with lumps or with filings. If there be any mysterious difference as to the capacity for heat in them, that will be shown during the process of solution. In general, in dissolving a metal in an acid, there is a development of heat; but if there were any difference in the quantity of heat which the lumps and an equal weight of filings contained when at the same temperature—that is to say, if heat could by any possibility be matter—there would necessarily have been a greater development of heat in one vessel than in the other. Had Rumford tried that one additional experiment, he would have had the sole credit of having established the non-materiality of heat.

27. Rumford found that, in spite of inevitable loss of heat in his operations (which consisted in boring a cannon with a blunt borer), the work of a single horse for two hours and twenty minutes was sufficient to raise to the boiling-point about nineteen pounds of water, besides heating the cannon and all the machinery engaged in the process. Here is his final reasoning:—

> "In reasoning on this subject, we must not forget to consider that most remarkable circumstance, that the source of heat generated by friction in these experiments appeared evidently to be *inexhaustible.*
>
> "It is hardly necessary to add, that anything which any *insulated* body or system of bodies can continue to furnish *without limitation,* cannot possibly be a *material substance.* It appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of

anything capable of being excited and communicated in the manner in which heat was excited and communicated in these experiments, except it be motion."

28. When we make a calculation from the data furnished by Rumford's paper, we find that, supposing heat to be a form of energy, and taking 30,000 foot-pounds per minute as the work of a horse, the mechanical equivalent of heat is 940 foot-pounds. The meaning of this statement is, that if you were to expend the amount of work designated as 940 foot-pounds in stirring a single pound of water, that pound of water at the end of the operation would be 1° Fahrenheit hotter than before you commenced. We can put it in another form, which is perhaps still more striking. In the fall down a cascade or waterfall 940 feet high there would be 940 foot-pounds of work done by gravity upon each pound of water; and therefore if all the energy which the moving water has as it reaches the bottom of the fall were spent simply in heating the water, the result would be that the water in the pool at the bottom of the fall would be 1° Fahrenheit hotter than the water at the top.

29. Davy first showed that by rubbing two pieces of ice together—by simply expending work in the friction of two pieces of ice—ice could be melted. Now a believer in the caloric theory would have argued thus: two pieces of ice when rubbed together cannot possibly melt one another, because in order to melt them heat must be furnished to them. But if the heat can only come from themselves when they are rubbed together, if it cannot come from surrounding bodies, they cannot possibly melt; because to melt one another they would have first to part with some of their heat.

To Davy's experiment, which seems to decide the question against the calorists, there was therefore this possible objection, that the heat might have come from some external source, so that he tried a second form of experiment. He rubbed two pieces of metal together, keeping them surrounded by ice, and in the exhausted receiver of an air-pump, so as to remove every possible disturbing cause, or even source of suspicion, from his experiment; and still he found that these two pieces of metal when rubbed together produced heat and melted the ice, every precaution having been taken to prevent heat from getting at them from every side.

30. It is curious that his reasoning upon the subject is extremely inconclusive, although his experiments themselves completely settle the question. He says :—

> "From this experiment it is evident that ice by friction is converted into water, and according to the supposition its capacity is diminished; but it is a well known fact that the capacity of water for heat is much greater than that of ice; and ice must have an absolute quantity of heat added to it before it can be converted into water. Friction, consequently, does not diminish the capacities of bodies for heat."

And there he stops. But some years afterwards he came to this conclusion from these experiments :—

> "Heat, then, or that power which prevents the actual contact of the corpuscles of bodies, and which is the cause of our own sensations of heat and cold, may be defined as a peculiar motion, probably a vibration, of the corpuscles of bodies tending to separate them. It may with propriety be called the repulsive motion. Bodies exist in different states, and these states depend upon the action of attraction and of the repulsive power on their corpuscles, or, in other words, on their different quantities of repulsion and attraction."

31. Davy explains by these experiments the difference between a solid and a liquid, and that between a liquid and a gas. In general the melting of a solid is produced by communicating heat to it. In other words, according to Davy's explanation, the particles of the solid are set in

vibration, and thus, in consequence of repeated impacts upon one another, push one another aside. And as he also says, you may consider this repulsive motion to have a complete analogy to the so-called centrifugal force in a planetary orbit, for the faster one particle is moving about another, the larger necessarily is the orbit into which it will be forced. The particles of a solid, then, are forced from one another by this repulsive action of heat, and it assumes what we call the liquid state. Increase still farther the amount of heat communicated to the body, the cohesive forces are at length wholly overcome, and you have free particles, as in a gas, flying about and impinging upon one another, but only for very brief periods coming near enough in the course of their gyrations to bring into play the molecular forces again. When, however, the molecular forces do come into play for a moment, you may have two particles adhering together, but they are soon knocked asunder by a blow from a third particle.

32. There is one other sentence, however, which must be quoted from Davy, for it shows when and how he finally got over his difficulties and confusion of reasoning. In 1812 he enunciated this proposition :—

> "The immediate cause of the phenomenon of heat, then, is motion, and the laws of its communication are precisely the same as the laws of the communication of motion."

When Davy was in a position to make that statement he had only to take it in addition to the second interpretation of Newton's third law (*ante* § 18), and the whole dynamical theory of heat was in his possession. Still, that publication of Davy's in 1812, like the earlier ones of Rumford and of Davy himself, remained almost unnoticed—looked upon, perhaps, as an ingenious guess, or something of that sort, but as something which it was not worth the trouble of philosophers to consider; and it was not until Joule's time, somewhere about 1840, that the subject was fairly taken up, and that justice was rendered to their real value.

33. Notice, however, how distinctly these two great leaders were men who based their work directly upon experiment. There is no *à priori* guessing, or anything of that kind, about either Rumford's or Davy's work. They simply set to work to find out what heat is. They did not speculate on what it might be. But both before and after their time there have been numbers of philosophers who have, without trying a single experiment, or at best trying only the roughest forms of experiment, endeavoured to discover by *à priori* reasoning what heat is.

34. The investigations of Colding and Joule, dating from about 1840, cannot here be treated in full; because, though it was to them that the final dethronement of caloric from its old position as an imponderable is unquestionably due, these exquisite experiments (especially those of Joule) extended to all forms of energy, and therefore included an immense range of subjects entirely beyond the scope of this work.

In so far, however, as they bear upon our present question, these researches re-established the conclusions of Rumford and Davy; and they supplied a much more exact determination of the *dynamical* (or, as it is commonly but inaccurately called, *mechanical*) *equivalent of heat* than that above deduced (§ 28) from some of Rumford's experimental data.

35. In fact the extensive, and exceedingly accurate, experiments of Joule led, in 1843 and subsequent years, by processes depending directly on friction, to numbers varying from 770 to 774 foot-pounds of energy as the equivalent

of one unit of heat (defined below, § 37) on the Fahrenheit scale. The number finally assigned by Joule (for the latitude of Manchester) is 772, and it is almost certainly not in error by anything approaching to 1 *per cent.*

In 1853 Joule verified this result by means of a very accurate determination of the specific heats of air, and a direct experimental proof (given in 1845) that the heat developed by the sudden compression of air is very nearly the equivalent of the work expended.

36. Direct measurements of the heat produced by the expenditure of mechanical energy were made in various ways by Colding, in 1843, and have been repeated in many forms by Hirn, Regnault, &c., since the publication (in 1849) of Joule's final result.

The direct verification of the fact that heat disappears when work is done by a heat-engine, unsuccessfully attempted by Séguin in 1839, was first effected by Hirn in 1857.

A great variety of indirect methods of approximating to the mechanical equivalent of heat have been successfully applied within the last thirty years by different experimenters. The earliest determinations of this kind are, of course, those of Joule, effected in 1843 and subsequent years, by means of magneto-electricity.

37. The results of all such experiments are briefly summed up in the exceedingly important statement known as the

First Law of Thermodynamics.—*When equal quantities of mechanical effect are produced by any means from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence or are generated.* And, in the latitude of Manchester, 772 foot-pounds of work are capable of raising the temperature of 1 lb. of water from 50° F. to 51° F.

38. Though by experiments such as those we have mentioned (but not, as yet, described or explained) Heat has been proved to be a form of Energy—whether kinetic or potential—we have made no progress towards the discovery of the mechanism upon which it depends.

And, referring again to §§ 30, 31, it may be stated generally that we have as yet very little information about the nature of the internal heat-motions, &c., of the particles of solids and liquids.

39. But we have obtained from several kinds of experiments, entirely different from these, what must be called a probable, rather than a plausible, explanation of the effects of heat on gases—along with at least a general idea of the nature of the motions upon which heat depends in such bodies. This idea, hinted at in § 31, is due originally to Hooke,* and (sixty years later) to D. Bernoulli; † but it has been resuscitated and immensely developed of late years by Herapath, Joule, Clausius, Clerk-Maxwell, Boltzmann, and others. It has been found capable of explaining a very great number of the known physical properties of gases: and it seems destined, in a comparatively short time, to acquire all the claims to acceptance which can be demanded from a physical theory of the motions, collisions, &c., of particles of matter whose exceedingly minute dimensions put them altogether and for ever beyond the range of the most perfect *possible* microscope.

40. From another absolutely distinct point of view we have obtained very remarkable information as to the nature of the motion upon which Radiant Heat depends. But here we are especially favoured, because we have complete experimental evidence that the nature and the mechanism of propagation of Radiant Heat are precisely the same as

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* *De Potentiâ restitutivâ*, 1678.

† *Hydrodynamica*, 1738.

those of Light (§ 3). Thus we have two quite independent sense-organs adapted for the study of these allied phenomena.

41. *Résumé of* §§ 20—40.—Heat is now *proved* to be a form of energy. Hence the *First Law of Thermodynamics*, which merely states the equivalence of heat to work, with the requisite numerical datum called *Joule's Equivalent.* The mechanism upon which heat-energy depends is (probably at least) approximately known so far as regards heat in a gas, and as regards radiant heat. Beyond these we have, as yet, little information on the subject.

42. **Effects of Heat.**—These are exceedingly varied and numerous, and in our present rapid sketch we cannot allude to any but the more common or more prominent of them. These we may classify as follows:—

a. Change of Dimensions, or of Stresses, in Solids; and of Volume, or of Pressure, in Fluids.
b. Change of Molecular State.
c. Change of Temperature.
d. Electric Effects.
e. Effects in *starting* Chemical Changes.

43 (*a*). The change of dimensions and stresses of solid bodies by heat is known by experience, even of the commonest kind, to every one. We mention a few instances taken at random, but it will be good exercise for the student to try to recollect others, and the same exercise will be found profitable in the other departments of this subject.

The "shrinking on," as it is called, of a wheel-tire, and of coil after coil on the core of a wrought-iron gun, is accomplished by heating the tire or coil, slipping it on while expanded by heat, and then cooling it suddenly or gradually as may be necessary.

Rails are not laid down end to end, but with a small interval; else on a summer day they might expand so much more than the ground supporting their bearings as to pucker, and displace one another.

The huge metal tubes of the Menai bridge are not rigidly fixed at each end, else they would tear themselves or their supports; they are free to expand and contract as their temperature changes, one end of each being supported on rollers.

Uncompensated clocks and watches (if their *average* rate be exactly adjusted) go too slow in summer and too fast in winter; the former simply, the latter mainly, on account of the change, by heat, of the dimensions of their moving parts. The touch of a finger on the graduated limb of a delicate meridian circle produces a perceptible change in the measured zenith-distance of a star.

A harp tuned in a warm room rises notably in pitch when taken out into frosty air.

Telegraph wires are *seen* to "sag" more and more as the temperature of the air rises.

Massive walls pressed outwards (by overloading of the roofs or floors of buildings) have been forcibly restored to their vertical position by the contraction of iron rods passed through them; nuts being screwed tight upon the rods up to the exterior surface, while the rods were in a state of expansion by heat.

44 (*a continuea*). The grand circulations constantly going on in the ocean and in the atmosphere are mainly due to the expansion of water and of air by heat. Bulk for bulk, the heated portions are lighter than the colder, and rise above them in virtue of the ordinary hydrostatic laws, which explain the floating of oil on water or the rise of a balloon in the air. On a smaller scale the rise of what we call *smoke*

from a chimney, ventilation of mines by a fire at the bottom of an "upcast" shaft, &c., are examples of the same effect.

45 (*b* and *c*). Take a piece of very cold ice. Though the assertion may appear a little startling at first, it is really a stone—just as much as is a lump of rock-salt or galena—only that its molecular or crystalline structure is somewhat more complex. It becomes warmer, just as other stones, by every fresh application of heat—*up to a certain point*, which we call its *melting-point*—but you cannot make it any hotter. Heat now does not change its temperature, but changes its molecular state. Precisely the same is true of the rock-salt only that the temperature of its melting-point is considerably higher than that of the ice.

Suppose sufficient heat to have been applied just to melt all the ice. It is still the same substance from the chemical point of view, its temperature is still that of the melting-point, but it is a liquid instead of a solid.

46 (*b* and *c continued*). Apply more heat to the water. Its effect is now to make the water warmer: in scientific language, the temperature of the water rises. Every fresh application of heat raises the temperature more and more till it reaches what is called the *boiling-point*, but here the rise of temperature again stops. Farther application of heat produces a new alteration in the molecular state, and the liquid changes into steam or water vapour.

47 (*b* and *c continued*). Suppose heat to have been applied till the whole of the liquid has, without farther rise of temperature, been converted into vapour—*saturated steam*, as it is technically called—we can now, by applying more heat, raise the temperature of the steam, so that it becomes what is called *superheated steam*, and is practically a gas. But this gas cannot be heated indefinitely farther without the production of another molecular change—this time what

is commonly called a chemical change—*dissociation:* the analysis or separation of the water-gas into its constituents, oxygen and hydrogen.

Experiment has not yet told us whether or not still farther applications of heat may be capable of altering the physical or chemical nature of either of these now merely *mixed* gases.

48. Thus the successive effects, produced by continuous application of heat to a piece of very cold ice, are—

1. Heating.
2. Melting.
3. Heating.
4. Evaporation.
5. Heating.
6. Dissociation.
7. Heating.

Water-substance is familiar to all, and, as we have seen, gives an excellent and instructive example of the various successive changes of state and of temperature. Few other substances offer, at least with our present very limited experimental facilities, so complete a series. On the other hand there are substances, such as *carbon*, which we cannot even melt; others, such as uncombined *hydrogen*, which, till the very end of 1877, we knew only in the gaseous form.

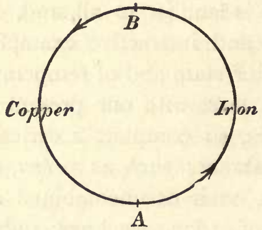
49 (*d*). Certain crystals, such as tourmalines, when heated attract other bodies in the same way as do sealing-wax or glass which have been electrified by friction. This is, however, still a very obscure branch of our subject, and has as yet yielded no results of great importance, though it may possibly become the source of enormous additions to our knowledge.

49 (*d continued*). But what is commonly called *Thermo-electricity* is already of immense practical as well as theoretical importance, as the reader will see when we come to the question of *measurement* of heat and temperature.

The fundamental phenomenon of Thermo-electricity is the following, discovered by Seebeck about 1820:—

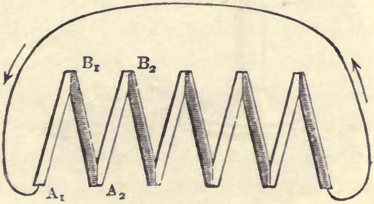
When one of the junctions of a closed circuit of two metals is raised to a higher temperature than the other, a current of electricity passes round the circuit and (in general) increases in intensity with increasing difference of temperature of the junctions. The direction of the current is, of course, reversed if the cold junction be now made the hotter.

If, for instance, the ends of an iron and of a copper wire be joined by twisting, soldering, or otherwise, we form what is called a *circuit* or re-entrant path, round which an electric current can travel.



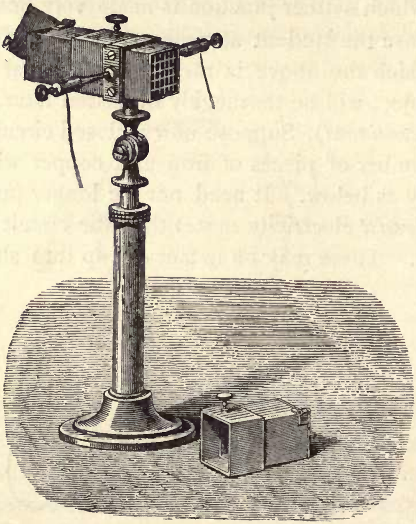
Let A and B in the sketch be the (necessarily) two junctions. To a person going completely round the circuit in the direction indicated by the arrows, these junctions would be distinguished from one another by the fact that, while at B he is passing *from iron to copper*, and at A *from copper to iron*, if he reversed the direction of his motion round the circuit, these characteristics of the two junctions would be *interchanged.* Now suppose the whole to be at any ordinary temperature, and a lamp flame to be applied (for a moment only) at A. A current of electricity will pass round the circuit in the direction of the arrows, and will continue, though becoming gradually weaker, till A at length cools down again, so as to have the same temperature as B. This is Seebeck's discovery. What we have just said as to the characteristic difference between the two junctions shows us that, if the lamp be now applied for a moment to B, the current produced will run round the circuit in the opposite direction to that indicated by the arrows. In fact, under the conditions specified, *the current passes from copper to iron through the warmer junction.* (This statement applies to all cases in which neither junction is made very hot. It would only confuse the student at present to give him the general law, of which the above is merely a particular case. The whole subject will be thoroughly discussed later.)

50 (*d continued*). Suppose now a closed circuit consisting of any number of pieces of iron and copper wire arranged alternately as below. It need not be longer (and therefore need not *resist* electricity more) than the circuit of two just described. These may be in fact cut up into shorter pieces



and re-arranged. Call the successive junctions in order A_1, B_1, A_2, B_2, &c. Then it is obvious that a person going round the circuit in the direction indicated by the arrows will at each A junction pass from copper to iron, and at each B junction from iron to copper. Hence all the A junctions, when heated, produce thermo-electric currents in the direction of the arrows. When the B junctions are all heated the current is the other way round.

But in the simple circuit we had only one hot junction, while we may have here as many as we please; it is obvious that by this arrangement we can increase the strength of the electric current (for the same difference of temperatures of the hot and cold junctions) in the same proportion as we increase the *total number* of junctions.



For convenience of application, the wires or rods A_1 B_1, B_1 A_2, A_2 B_2, &c., are made of equal length, and packed together as closely as possible into what is called a *Thermo-electric Pile*, so that all the A junctions are at one end and all the B junctions at the other. Thin paper, gutta percha, or other insulating material, is interposed between each two contiguous rods to prevent their touching one another, except where they are soldered together at the junctions. It has only to be added that as Seebeck (led by very curious reasoning) discovered that the currents produced by alternate bars of bismuth and antimony are far more powerful than those produced under the same circumstances of temperature and resistance by iron and copper—the pile is generally built up of alternate bars of the former pair of metals. The invention of this valuable instrument is due to Nobili (1834).

51 (*e*). There is little doubt that it is the heat developed by friction which inflames the particles of iron when the old "flint and steel" is used, just as it sets fire to amorphous phosphorus in contact with chlorate of potash in our modern "safety matches"; or as the heat of a red-hot poker causes gunpowder to explode. In all such cases heat appears to *induce* or *promote* chemical combination; to perform, in fact, the reverse of the operation which we have already attributed to it as dissociation (§ 47).

52. **Measurement of Heat and of Temperature.**—The absolute distinction between the ideas of heat and of temperature cannot be too soon learned by the student. Heat, we have seen, is a REAL SOMETHING, a form of energy. Temperature he may be content at first to look on as a mere *condition* which determines which of two bodies put in contact shall part with heat to the other. That such a statement is consistent with observed facts is shown by this, that if A is at the same temperature as B and also at the same temperature as C—no transfer of heat takes place between

B and C, whatever be these bodies : i.e. *bodies which have the same temperature as another body have themselves the same temperature.*

To refer to one of the analogies formerly employed, Heat may be compared to the quantity of air in a receiver, temperature to the pressure of that air. When two receivers, each containing air, are connected by a pipe, air is forced to pass from the receiver in which the pressure is the greater to that in which it is less. And this is altogether independent of the quantities of air in the two receivers :—that which parts with some of its air may be very small in comparison with the other, and contain far less air ; it is the difference of pressure alone which determines the direction of the transfer.

53. But, just as one receiver may be more capacious than another, so as to contain more air at a given pressure—so one body may have more *capacity for heat* than another, and therefore contain more heat even when their temperatures are the same.

And this difference of capacity may be due in part either to mere quantity of matter, (as when we compare an ocean with a pond,) or to a specific property of the substance itself—for, as we shall see later, mass for mass, water has thirtyfold the capacity for heat that mercury has. This specific property is known by the name of *Specific Heat*, a term derived from the old erroneous notions as to the nature of heat, but now fairly rooted in the language so as to be almost permanent, though as much calculated to mislead the student as is the celebrated "*Centrifugal Force.*"

54. Thus the quantity of heat employed in the entire system of fires, furnaces, &c., of Great Britain during a whole year—producing vivid incandescence of millions of tons of coal and of liquid iron—may be a mere trifle compared with the heat required to raise the average

temperature of the Atlantic Ocean by a single degree of the thermometer.

55. Referring again to the general principle enunciated in § 9, it is clear that we may measure heat in terms of a *unit of heat*, which may be defined as the heat required to melt a pound of ice at the freezing-point, to raise to the boiling-point a pound of ice-cold water, or in general *to produce any definite physical change in a given mass of a given substance.* Or, knowing as we do, that heat is a form of energy, we may dynamically measure a quantity of it by the number of foot pounds of work to which it is equivalent (§ 37).

But the mode usually adopted in Britain is to define a *unit of heat* as the amount of heat required to raise a pound of water from the temperature called 50° F. to that called 51° F.

56. Of course we may equally well adopt what are called *metrical* units, and the scale of the Centigrade Thermometer instead of that of Fahrenheit, but the change from one of these systems to another is one not of principle but of convenience, and, at the worst, involves a mere arithmetical operation of multiplication or division by a definite number. Such questions rarely rise to *scientific* importance, though they may raise (often justly) discussions as to comparative convenience.

[Thus, there can be no question about the fact that the *mètre* is inconveniently long, and the *kilogramme* inconveniently massive, for the ordinary affairs of life.

The average length of the arms of shop-girls, and the average quantity of tea or sugar wanted at a time by a small purchaser, have no conceivable necessary relation to the ten-millionth part of the quadrant of the earth's meridian passing through Paris or the maximum density of water.

But the standard *yard* and *pound* were, no doubt, originally devised to suit these very requirements as regards the average dimensions of the shop-girl or the paying powers of the ordinary customer. Yet this invaluable superiority of our *units* over those of the metrical system is, with an almost over-refinement of barbarism, thrown away at once when we come to multiples or submultiples. The very lowest attempt at consistency should have rendered it impossible for any one who employs the decimal notation to use any but a decimal system of multiplication and subdivision of units. All the monstrosities of the old Logic with its *Barbara celarent*, &c., or of the Latin Grammar, with its *As in presenti*, &c., seem almost natural and proper when compared with a statement like this :—

12 inches = 1 foot, 3 feet = 1 yard, 220 yards = 1 furlong, 8 furlongs = 1 mile.

And even this is nothing to the awful complex of poles or roods, grains Troy and Avoirdupois, drachms and fluid ounces.]

57. The measurement of *Temperature*, upon which we have seen (§ 52) that the measure of Heat ultimately depends, presents absolutely unlimited choice.

Any of the *effects* of heat (which we have already briefly discussed) may be employed, and we may use any material substance whatever for the purpose.

It will be seen, however, when we have passed these preliminaries, that the *Second Law of Thermo-dynamics* enables us to lay down an ABSOLUTE definition of temperature :—absolute in the sense that it is entirely independent of the physical properties of any particular kind of matter, and depends solely upon the laws of transformation of energy.

58. It will at once be obvious to the reader that, since

there is such an absolute scale of temperature, it must be adopted in all really scientific reasoning from the results of experiments; though it may happen to be very difficult to apply it directly, during the practical work of experiment and observation.

59. Few experimental measurements, certainly very few in which great precision is sought, are made in terms of the scientific or other units to which they are ultimately reduced. Thus, in constructing a screw micrometer for delicate astronomical or other measurements, it is not necessary, even if it were practicable, to give the screw *exactly* 10 or 100 threads to the inch. What is necessary is a good, *i.e.* a uniform, screw:—and the exact length of its step is of no consequence. When the observer has, once for all, measured with it a number of objects or angles of known magnitude, he knows the *value of one whole turn*, and thence the value of any reading whatever, by a simple arithmetical process.

Very fine thermometers, for research, often have their tubes not only calibrated, but *graduated* before the bulbs are blown on them. The freezing and boiling-points are then determined with the utmost care in terms of the arbitrary scale of the instrument, which thus (by an arithmetical operation) becomes perfectly definite throughout.

Far from being a drawback to the use of such an instrument, the arbitrary scale is often of positive advantage to the experimenter, for it prevents his being (as the most honest and careful experimenter is very liable to be) unconsciously influenced by a knowledge of the reading that is to be expected. And the mere arithmetical difficulty of passing from one scale to another is so trifling in comparison with the difficulties of experiment that it would be wholly disregarded, even were there not the distinct gain thus secured, of absolute freedom from the bias of preconceived notions.

60. What we want at present, in our preliminary sketch of the subject, is not the rigorous scientific measure of temperature, but something which shall be at once easy to comprehend and easy to reproduce, and which shall afterwards require only very slight modifications to reduce it to the rigorous scale.

Approximately pure water is (practically) to be obtained with ease everywhere. Now our fundamental principle (§ 9) assures us that the changes called melting and boiling will always take place, with the same substance, each under its own precise set of conditions.

It will be found later that the only conditions which require to be insisted on here are those of temperature and pressure. Hence we merely *assert* for the present, that

For a definite pressure there is a definite temperature at which pure ice melts, and another definite temperature at which pure water boils.

61. The idea of using two such fixed temperatures for determining a scale is due to Newton.

For our present purpose we may suppose we have one vessel in which ice is melting, and another in which water is boiling, the barometer standing at 30 inches.*

If we call the temperature of the cold water zero, or 0°, that of the boiling water 100°, we adopt what is called the *Centigrade* scale.

Now it is obvious that we may obtain every possible intermediate temperature by mixing portions of water from the two vessels in different proportions. And we may

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* The student may here take for granted that it would only confuse him were we now to give the scientifically rigorous definition of the temperature called the "boiling-point."

define the intermediate degrees by saying that the percentage (by bulk or preferably) by weight of the hot water in each such mixture is its temperature in degrees. Thus 10° C. would be the temperature of a mixture of 10 lbs. of water at 100° C. with 90 lbs. of water at 0° C., and so on. This is obviously but one of an infinite number of ways in which the intermediate degrees might have been defined; but it has the advantage of directness and simplicity, while it is near enough to the absolute scale for our present purposes. And it has the farther advantage that it is the only one upon which the temperature of a mixture of equal weights of water at any two temperatures has a value exactly halfway between these.

Until we can point out clearly the necessity for, and the possibility of, making improvements on this scale, we shall employ it for our work; for it accords so closely with the absolute scale that careful experiment is required even to show that it does not exactly coincide with it.

62. The effect of heat which is most commonly employed for measurements of heat and temperature is the change of volume of liquids (§ 42). We may take for granted that every reader has some little familiarity with an ordinary *Thermometer*. The liquid employed is usually mercury or alcohol. The precautions necessary in making and using Thermometers will be discussed later. The other effect of Heat most commonly employed for these purposes is the Thermo-electric one already described. (§ 49).

In two respects it is vastly superior to any of the others—for, *first*, it is far more delicate; and, *second*, its indications can quite easily be made visible to the largest audience.

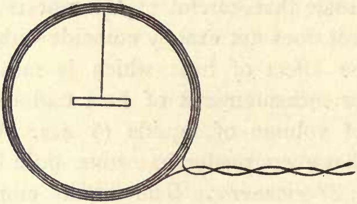
This method is based on the fact that, at least for a small difference of temperatures of the junctions, the strength of the electric current is directly proportional to that difference.

Hence a galvanometer, an instrument which measures the strength of the electric current, measures at the same time the difference of temperatures of the junctions.

63. Here a digression is necessary. The fundamental fact of Thermo-electricity (§ 49) belongs directly to our subject; but the fundamental fact of Electro-magnetism, on which the action of the galvanometer depends, is entirely foreign to it.

The fact, discovered by Oersted in 1820, is simply that *the position of a freely suspended magnet is, in general, altered by the passage of an electric current in its neighbourhood.*

The figure represents all the essential features of the only form of this experiment which we require for illustration.



A long copper wire, covered with silk or gutta-percha, to prevent contact of the wire with itself or with other metal, is wound into a circular coil of a considerable number of turns, and its free ends are connected—one with a zinc, the other with a copper plate. The coil is placed vertically in the magnetic meridian, and a magnetized steel bar is suspended horizontally inside it by a fine silk thread. While the zinc and copper plates are dry, and not in metallic contact, the magnetized bar of course takes the line of magnetic north, and therefore settles in the plane of the coil. But the moment the zinc and copper plates are dipped into a vessel containing water slightly acidulated, so as to cause an electric current to pass round the coil, the magnet is deflected, and tends, so far as it can, to set itself at right angles to the plane of the coil. As the figure is drawn above, the bar tends to turn one or other end towards the spectator.

The actual position which it will finally take up depends upon the relative amounts of the forces exerted upon it by the earth's magnetism and by the electric current. If the current be very weak the magnet is very little deflected; if the current be very strong the magnet is placed almost at right angles to the plane of the coil. Thus, from the *amount* of the deflection, the *strength* of the current may be calculated. The *direction* in which the current passes round the coil determines *to which side* of the coil the north pole of the magnet will be deflected. This can easily be shown by interchanging the copper and zinc plates, when we find the direction of the deflection reversed. The rule which is found to determine the direction of the deflection may be stated thus. Suppose that, in the figure, we are looking at the coil from the west side, then the left-hand end of the magnet is what is usually called its north pole. If, then, the current be so applied that positive electricity passes round the coils of wire in the direction in which the hands of a watch move, the north end of the magnet will move towards the *east* side of the coil, *i.e.* will move away from the spectator.

64. The galvanometer is usually constructed on a small scale, because the action of the current on the magnetic poles within the coils is greater as their radius is smaller (provided

there be the same number of coils and the same strength of current). Also a small magnet has greater mobility; and in general harder temper, so that it preserves its magnetization longer than a large one. Hence a double advantage is gained by diminishing, as far as possible, the dimensions of the apparatus. Another gain is thus insured: the number of coils, and with them the electro-magnetic action, may be greatly increased while the *length* of the wire, which by its resistance weakens the current, may actually be reduced. But all the more essential features of galvanometers are exhibited in the rude apparatus depicted in § 63.

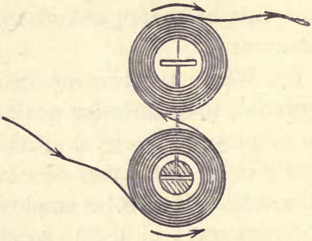
65. Suppose, now, a small mirror to be fixed vertically to one side of the magnetized bar, and a ray of sunlight to be made to fall on it, and after reflection received on a white screen. Every motion of the magnet would be at once indicated by the corresponding motion of the illuminated spot on the screen. And the farther off the screen is placed, the greater will be the motion of the spot for the same deflection of the mirror—*i.e.* of the magnet. Thus deflections, however small, may be magnified so as to become visible even to a very large audience. This makes the thermo-electric method invaluable for lecture-illustration. And here a fourth important advantage is gained, for the smaller the deflections of the magnet, the more nearly are they proportional to the strength of the current.

When accurate measurement is our object, the little mirror is made concave, and a wire is adjusted vertically between the mirror and the source of light at such a distance that a sharp image of it is formed on the screen. This, and not the ill-defined patch of light which it crosses, serves as an index, by which to read the deflections by the help of the scale of equal parts drawn on the screen.

66. The various successful devices for rendering galvano-

meters more and more sensitive, belong properly to the subject of electricity; but it may be well to indicate here a few of the more important.

The mirror, with a number of very small pieces of hard steel (magnetized to saturation), attached to it, need not weigh more than a fraction of a grain. It is supported by a *single fibre* of unspun silk. The coils of wire should be as numerous, and of as small diameter as possible, to secure the greatest effect (§ 64); but the whole resistance of the wire should be as small as possible—since in the greater number of thermo-electric arrangements which we require for radiant heat, &c., the *main resistance* is in the galvanometer coils. Thus the best copper should be employed, and the diameter of the wire should be so small as to allow of a great number of coils of small diameter, while not so small as to destroy this gain by the greater consequent resistance, and weakening of the current.



The *astatic* principle may also be introduced with great advantage for very delicate instruments. Here two light needles, or sets of needles, are placed parallel to each other with their north poles oppositely directed, and their middle points connected by a thin aluminium wire, which is supported in a vertical position by a fibre of unspun silk.

Each magnet has its own coil, and the ends of the wires are so connected, that (as in the figure) a current, passed through them, runs round them in opposite directions. Thus, as the direction of the current, as well as the direction of the north pole, are *each* reversed in passing from one coil to the other, the electro-magnetic effects tend in the *same* direction, while those of the earth's magnetism tend in *opposite* directions.

If we could make the magnetic moments of the needles exactly equal, and place them with their magnetic axes exactly parallel, terrestrial magnetism would not affect the apparatus at all, and the electro-magnetic effect would be counteracted and balanced solely by the torsion of the silk fibre. Practically this cannot be done; but the effective directive force of the earth's magnetism can easily be reduced to $\frac{1}{100}$th of its whole amount, and even less; thus securing at least a hundredfold greater delicacy by this arrangement.

As an illustration of the delicacy thus attainable, it may be mentioned that it is easy to construct a galvanometer which will show the $\frac{1}{1000}$th or even the $\frac{1}{10000}$th of a degree Fahrenheit of difference of temperatures beween the two junctions of a copper-iron circuit (§ 49) at ordinary temperatures.

67. When a galvanometer is to be used sometimes for powerful, sometimes for weak currents, various devices may be employed; such as making the coil in two or more nearly equal parts, one or more of which may be employed at a time. If two be employed, with the current running opposite ways in them, a much more powerful current will obviously be required to produce a given deflection than if it run the same way in both.

Another device is to use external, adjustable, magnetized bars so as to increase or diminish at pleasure the intensity of the field of force due to the earth's magnetism. This method is satisfactory for powerful currents, but not for weak ones, because the earth's horizontal magnetic force is continually and rapidly changing, and when the greater part of it is neutralized, even a slight change may produce great *percentage* variation in the uncompensated part, on which alone the delicacy of the galvanometer depends.

The great majority of those valuable improvements just described, were recently introduced by Sir W. Thomson (originally for practical telegraphic applications). Another, and by no means the least, consists in inclosing the magnets and mirror in a small, narrow, glass cell, with parallel faces. The viscosity of the air, and the large surface and small moment of inertia of the mirror, cause this instrument to pounce almost instantly upon its exact reading, without the long-continued and tantalizing oscillations which were unavoidable in the older instruments. This *dead beat* principle, as it is called, enables the experimenter to make accurate readings faster almost than he can record them; and this not only effects an immense saving, both of time and trouble, but enables the observer *to study a phenomenon in various ways before it has sensibly changed its conditions*, a most desirable thing in itself, but only now made possible.

68. **Sources of Heat.**—As heat is only one of the many forms of energy, and as any one form of energy can in general be transformed, in whole or in part, into another, the sources of heat are as numerous as the forms of energy at our disposal. Our available sources of potential energy are mainly fuel. Under the head of fuel are included not merely coal, wood, and so on, but also all that may properly be called fuel — the zinc used in a galvanic battery, for instance, and various other things of that kind, including the food of animals.

We have also :—

Ordinary water-power.
Tidal water-power.

In the kinetic form we have :—

Winds.
Currents of water, especially ocean currents.
Hot springs and volcanoes.

There are other very small sources known to us, some exceedingly small, such as diamonds for instance; but those named include our principal resources. And every one of these, by proper processes, can be made a *Source of Heat.*

69. Now comes the question, What are the sources of these supplies themselves? They also can be classified under four heads.

The first is *primitive chemical affinity*, which we may suppose to have existed between particles of matter from the earliest times, and still to exist between them, because these portions of matter have not combined with one another nor with other matter. If, for instance, while the materials of which the earth is composed were widely separated from one another, there were particles of meteoric iron and native sulphur which, when the materials fell together to form the earth, did not combine, but still remain separate from one another, the mutual chemical potential energy of the iron and sulphur remains to us as a portion of energy primordially connected with the universe. But of that, so far as we know, at least near the surface of the earth, there is very little. There may be towards the interior enormous masses of as yet uncombined iron and uncombined sulphur, or various other materials; but towards the surface, where they could be of any direct use to us, the quantities of these are excessively small.

The second source is *solar radiation*, by far the most abundant source we have. Then we have two very instructive forms, *the energy of the earth's rotation about its axis*, and *the internal heat of the earth.*

70. Now compare our available stock with the sources from which we derive it, and we easily see how the two are connected.

Our supplies of fuel are almost entirely due to the sun. In times long gone by, the sun's rays by their energy, as absorbed in the green leaves of plants, decomposed carbonic acid and stored up the carbon. That carbon, and various other things stored up ages ago along with it, we have still as an immense reserve fund of coal.

For food we are mainly indebted to the sun again, because the food of animals must ultimately be vegetable food, even of the animals which live upon animal food. For ordinary water-power we are also indebted to the sun, because it is mainly the energy of the radiation from the sun which evaporates water from the plains or seas, so as to be condensed again at such an height that it has potential energy in virtue of its elevation. Ordinary currents of water are a mere transformation of this potential energy, because water on a height converts part of its potential energy into kinetic energy of visible motion as it flows down.

But when we come to tidal water-power, we must look to another source. If we employ tidal power for the purpose of driving an engine, we take it in the rise of the water as the tide wave passes us. We secure a portion of water at a certain elevation, wait till the tide has gone back, and then take advantage of the descent of that portion of water. Now, if we were to go on doing this for any considerable period of time, and over large tracts of sea-coast, we should find that the effect would be to gradually slacken the rate of rotation of the earth.

Winds and ocean currents are almost entirely due to solar radiant heat. And hot springs and volcanoes, which have never been employed for any direct production of work, depend mainly, at least, upon the internal heat of the earth; partly, perhaps, on potential energy of chemical affinity.

71. It is obvious, then, that the sun is the great source of almost all our available energy; and we can carry the investigation still one step farther back, so as to inquire into the source of the sun's enormous store of energy. It will be seen later, that no known chemical source can account for more than a very small fraction of it; and that the only adequate known source is the potential energy which its parts must have possessed, in virtue of their mutual gravitation, while they were widely dispersed throughout a space of dimensions at least equal to those of the known solar system.

72. **Transference of Heat.**—Under this head it is usual to classify as the three ways in which heat can be transferred from one place to another, the processes of

Conduction.
Radiation.
Convection.

As will be seen presently, this list involves some confusion, for as commonly understood it includes either too much or too little.

73. By *Conduction of Heat* we usually mean that comparatively slow transfer of heat from part to part of a body, or from one body to another with which it is in direct contact. It is mainly by conduction that any part of the earth's internal heat reaches the surface, and that the sun's heat penetrates into the crust. The study of the laws of conduction, and of the relative conducting powers of

various substances, as well as of the conducting power of one and the same substance at different temperatures, is of very high practical value, as well as of intense scientific interest.

By *Radiation of Heat* we usually mean the process by which heat is transferred from one body to another with the velocity of light—even through space altogether devoid of what is called tangible matter. It is entirely by radiation that we obtain heat from the sun, as also (in very small quantity) from other stars. The subject of radiation and the connected subject of absorption have, of late, received unexpectedly an enormous extension. The practical process of *Spectrum Analysis*, to which they have recently led, is one of the most important means at our command for the study alike of the most distant stellar and nebular systems, and of the almost inconceivably minute grained structure of matter.

By *Convection of Heat* is usually meant the carriage of heat-energy from one locality to another *along with* the particular portion of matter with which it is associated. The Gulf-stream is a vast convection-current, whereby the solar heat of the tropics is carried into the North Atlantic. Every form of ventilation, whether of coal-mines or of private houses, at least if heat be directly the effective agent, is a mere case of convection.

74. To avoid what the student might feel to be perplexing novelties, it may be well to adhere in this *elementary* book to the classification just given. But it may not be amiss to make here a remark or two upon it.

In the first place we have absolutely no proof that radiation from the sun is in any of the forms of energy which we call heat, while it is passing through interplanetary space. That it is a form of energy, and that it depends upon some species of vibration of a medium, we have absolute proof.

But it seems probable that we are no more entitled to call it heat than to call an electric current heat; for, though an electric current is a possible transformation of heat-energy and can again be frittered down into heat, it is not usually looked upon as being itself heat. Just so the energy of vibrational radiations is a transformation of the heat of a hot body, and can again be frittered down into heat—but in the interval of its passage through space devoid of tangible matter, or even while passing (unabsorbed) through tangible matter, it is not necessarily *Heat.*

Again, in dealing with Thermo-electricity, we shall find that a current of electricity has a convective power for heat:—*i.e.* that when passed through a metal bar whose temperature is not the same at all points it may carry heat from the hot to the colder parts, or *vice versâ;* and that when passed through a circuit, made up partly of one metal, partly of another, and at the same temperature throughout, it carries heat from one of the two junctions to deposit it in the other.

These facts render the usual hard and fast classification of § 72 somewhat inadequate; but without farther adverting to this we merely mention that the apparent exceptions can easily be treated under the head of *Transformations of Heat*, as will be seen when we go over the various divisions of the subject more fully. This is clearly a case of somewhat illogical arrangement, but, as already explained (§ 11), we have decided to adopt it, lest we should perplex rather than assist the beginner. The student who has got successfully over the earlier stages will easily surmount this difficulty also.

75. **Transformations of Heat.**—These are, of course, as numerous as the other forms of Energy, since we have already seen that any form of energy can be transformed (at

least partially) into any other. On this point nothing farther need be said at present. But there is another point of the case which is of the utmost importance. We may state it thus :—

Given a certain quantity of energy in one form and under given conditions, how much of it can, by means of a given kind of apparatus, be converted into some other definitely assigned form, the rest being either untransformed, or transformed, in whole or in part, into some third form?

76. Now part at least of the enormous amount of waste which takes place in an ordinary steam-engine is familiar to all. Not to speak of the unburned fuel which is allowed to escape as smoke, the very ascent of the column of smoke is due to wasted heat, and there is constant and large leakage from the furnaces, boilers, and cylinders. The very fact that the stoke-hole is so intolerably hot is due to the same waste. But there is unavoidable as well as unnecessary waste. It has been satisfactorily demonstrated that in the very best engine, even if it were theoretically perfect, and working at ordinary ranges of temperature, only somewhere about one-fourth—very rarely so much, but at the best about one-fourth—of the heat which is actually employed is converted into work; that is to say, three-fourths of the coals, or three-fourths of the heat employed, are absolutely wasted under the most favourable circumstances. What is it that determines this? Why is it that the whole of a quantity of work or of potential energy can be converted into heat, while the heat cannot be converted again, except in part, into the higher form of work or potential energy?

77. The answer is included entirely in the word "higher," just used. When energy is to be converted from a higher form into a lower, the process can in general be carried out

in its entirety; but when it comes to be a question of reversal —going up hill, as it were—then it is only a fraction, in general (even under the most favourable circumstances) only a small fraction, of the lower kind of energy which can be raised up again into the higher form. All the rest usually sinks down still lower in the process. When it is low already, and part of it has to be elevated and transformed into a higher order, a large part of it must inevitably be still farther degraded; in general the larger part of it. This is one of the most important advances ever made in science, and has most stupendous bearing on the future of the whole visible universe.

78. In all transformations of energy we find experimentally that there is a tendency for the useful energy to run down in the scale,—so that, the quantity being unaltered, the quality becomes deteriorated, or the availability becomes less; and thus we are entitled to enunciate, as Sir William Thomson did very early after the new ideas were brought into full development, the principle of Dissipation of Energy in Nature.

79. The principle of dissipation, or degradation, as it may perhaps preferably be called, is simply this, that as every operation going on in nature involves a transformation of energy, and every transformation involves a certain amount of degradation (degraded energy meaning energy less capable of being transformed than before), energy is as a whole continually becoming less and less transformable.

80. Thus, as long as there are changes going on in nature, the energy of the universe is falling lower and lower in the scale, and we can at once see what its ultimate form must be, so far at all events as our knowledge yet extends. Its ultimate form must be that of heat so diffused as to give all bodies the same temperature. Whether this be a high

temperature or a low temperature does not matter, because whenever heat is so diffused as to produce uniformity of temperature, it is in a condition from which it cannot raise itself again. In order to procure any work from heat, it is absolutely necessary to have a hotter body and a colder one. When therefore all the energy in the universe is transformed into heat, and so distributed as to raise all bodies to the same temperature, it is impossible—at all events by any process yet known, or even conceivable—to raise any part of that energy into a more available form. *Why* it is so, and *what* (slight) exceptions there are to this general statement, will form an important subject for discussion farther on. For the present purpose we may hold it as a perfectly general law of nature.

81. The grand question, therefore, with regard to all transformations of energy is *To what extent can they be carried out?* This, of course, is a question to which nothing but experiment, or reasoning ultimately based on experiment, can possibly give an answer. And, so far at least as the transformation of heat into work, and various allied transformations, are concerned, it has been answered in the most brilliant and satisfactory manner.

82. Perhaps no purely physical idea has done so much to simplify science, or led to so many singular and novel predictions (subsequently verified by experiment) as has Carnot's idea of a *Cycle*, or his farther idea of a *Reversible Cycle*, of operations.

It has supplied not merely the legitimate mode of finding the relation between the heat taken in and the work done by an engine, but also the test of perfection for a heat-engine, an absolute definition of temperature, the effect of pressure on the melting-points of solids, and innumerable important groups of associated properties of matter and energy under various conditions. To a great extent these are included in the statement of the

Second Law of Thermodynamics.—*If an engine be such that, when it is worked backwards, the physical and mechanical agencies in every part of its motions are all reversed* (see § 89), *it produces as much mechanical effect as can be produced by any thermodynamic engine, with the same temperatures of source and refrigerator, from a given quantity of heat.*

83. It is to be particularly observed here that *Reversibility* (see §§ 88, 89) is the sole test of perfection of an engine. Also in the working of a reversible heat-engine nothing is said about the nature of the working substance; the temperatures of source and refrigerator, and the quantity of heat supplied, are the sole determining factors of the work which can be done. The importance of this proposition, as regards actual and proposed engines, cannot be over-estimated.

84. Carnot's work is upon the *Motive Power of Heat*, and was published in 1824. It forms no inconsiderable portion of Sir W. Thomson's many scientific claims that he recognised at the right moment the full merits of this all but forgotten volume, and recalled the attention of scientific men to it in 1848; pointing out, among other things, that it enabled us to give, for the first time, an *absolute* definition of *Temperature*. Although Carnot (seemingly against his own convictions) reasons on the assumption that heat is matter, and therefore indestructible; and although, in consequence, some of his investigations are not quite exact, his work is of inestimable value, because it has furnished us, not only with a correct basis on which to reason but, with a physical method of extraordinary novelty and power, which enables us at once to apply mathematical reasoning to all questions of this kind. These, then, are his two great claims—first, the setting thermo-dynamics upon a proper

physical and experimental basis; and, second, in the furnishing us with a means of reasoning upon it which was absolutely new in physical mathematics, and which has been, not merely in Carnot's hands, but in the hands of a great many of his successors, as fruitful in new discoveries as the idea of the conservation of energy itself.

85. In order to reason upon the working of a heat-engine (suppose it for simplicity a steam-engine), we must imagine a set of operations, such that at the end of the series the steam or water is brought back to the exact state in which it was at starting. That is what Carnot calls a cycle of operations, and of it Carnot says, that only for such a cycle are we entitled to reason upon the relation between the work done and the heat spent. If a quantity of steam were allowed merely to expand, losing heat in the process and doing work, we should have no right whatever to say that the quantity of heat which has disappeared is the equivalent of the work which is given out, because at the end of the operation the steam is in a different state as to pressure and temperature from that in which it was at the beginning. It was saturated steam at a certain temperature, let us say, to start with, and at the end of the operation it may still, if proper adjustments be made, be saturated steam, but it is necessarily at a different temperature, and therefore we have no right to assume that it possesses intrinsically the same amount of energy as it did in its former state. We have no right whatever to reason upon the quantity of heat which appears to have gone, as compared with the work which has been done, when the working substance begins in one state and ends in another. But if we can by any process bring the working substance back to its initial state, then we are entitled to assert that it must contain neither more nor less

than it did at first, and therefore of course we are also entitled to reason upon all the external things that have taken place during the operation, and to determine the condition of equivalence among them.

86. The hypothetical operation which Carnot introduced for the purpose of reasoning on this subject is, like most great ideas, excessively simple—*when found.* Let us imagine two bodies, each maintained constantly at a definite temperature. These will be called the hot body and the cold body respectively. In addition to these suppose a body which, as regards other bodies, is neither cold nor hot, being incapable of absorbing heat or of giving it out—a non-conductor of heat. Suppose the walls of the working cylinder and the piston to be non-conductors of heat, but the bottom of the cylinder a perfect conductor. Suppose water and steam (in proper proportions (§ 391)) to be in the cylinder, both at the same temperature, that of the cold body. Place the cylinder on the non-conductor and expend work in pressing down the piston, the contents will become warmer, and some steam will be liquefied. Continue this process till the temperature rises to that of the hot body—then transfer the cylinder to it. Now allow the piston to rise, the contents remain at the temperature of the hot body, fresh steam is generated, and work is done. Arrest this process at *any* stage and transfer the cylinder to the non-conducting body. If we now allow the contents farther to expand, more work is done, but the temperature gradually sinks. Continue this process till the temperature falls to that of the cold body, to which, therefore, without loss or gain of heat, it may now be transferred. Next apply work to compress it at the constant temperature of the cold body till (by condensation) the contents have become exactly as they were at starting. The cylinder must now be transferred

to the non-conducting stand, and everything is as it was at first—save that some heat was taken from the hot body in the second operation, and heat was given to the cold body during the fourth. Also it is evident that *more* work has been done during the second and third operations than was spent in the first and fourth, for the temperature, and therefore the pressure, of the contents was greater during the expansion than during the compression. Of course this operation may be repeated any number of times.

87. Notice particularly what the peculiarity of the operation is. The steam or expanding substance, whatever it is —for air or anything else would do equally well—must always be in contact with bodies at its own temperature, or else with non-conducting bodies. If it were in contact with a body of a lower temperature, there would be a waste of heat. Heat would pass by conduction from the cylinder to external bodies, and would of course be wasted as regards work. The same would happen if the cylinder were to be removed from the non-conducting body and placed upon the cold body, before its contents had been allowed to expand sufficiently to cool down to the temperature of the cold body: some heat would then be conducted away at once, and be lost to the engine. So, throughout the whole of Carnot's operations, it is essential that there should be no direct transfer of heat at all except while heat is being taken in from the hot body or given out to the cold body: the temperature of the contents of the cylinder being in each of these cases (all but exactly) the same as that of the body with which they are for the moment in contact.

88. We now come to another point, also perfectly novel, and of great importance. Suppose the operations in Carnot's cycle to be performed in exactly the reverse order. Begin, for instance, with the hot body, but do not allow the piston

to rise there. Take the cylinder from the hot body when the water and the steam below the piston have acquired the higher temperature. Lift it to the non-conducting body, and then allow the piston to rise. Let it continue to rise, doing work all the time, till the temperature sinks to that of the cold body; place it on the cold body; allow the steam to expand still farther,—it will be in that case giving out work but taking in heat. When it has risen to its former highest point, place it back again on the non-conducting body, force the piston back to the same extent as that to which it rose when (in Carnot's direct set of operations) it was first placed on that body. Everything has taken place in precisely the reverse order to that in which it took place before. Finish then upon the hot body, and press home. There is sent back in that final operation precisely the quantity of heat taken from the cold body; but during the two first operations the piston was in contact with steam at a lower temperature, and therefore at a lower pressure than during the two last. And, therefore, in the reversed method of working the engine, work has on the whole to be spent in taking heat from the cold body and depositing it in the hot body.

89. These are the grand ideas which Carnot introduced. Their two distinctive features are, *first*, the idea of a complete cycle of operations, at the end of which the working substance, whatever it is, is brought back to precisely its primary condition;—this cycle can be repeated over and over again indefinitely. *Secondly*, the notion of making the cycle a reversible one, so that all the operations can be performed in the reverse order; *i.e.* instead of taking in heat at any stage, heat is given out;—instead of work being done by the engine at any stage, work is spent upon it. With these reversals of each part of the

operation, the whole cycle can be gone over the reverse way.

90. Now Carnot, considering heat as a material substance, says that obviously it has done work in the direct series of operations by being let down from the higher temperature to the lower, just as water might do work by being let down through a turbine or other water-engine, doing work in proportion to the quantity that comes down and the height through which it is allowed to descend. In the reversed operations work is spent in pumping up the heat again from the cold body to the hot one. Here it is of course assumed that the quantity of heat which reaches the condenser is the same as that which leaves the boiler;—*i.e.* virtually that heat is *matter*, and therefore unchangeable in quantity. We now know that this notion of the nature of heat is erroneous, but Carnot's reasoning does not therefore lose its value, because the change of a word or two only is required to render it perfectly applicable with our modern knowledge of the subject.

91. One point which appears to show conclusively that Carnot's analogy (not his result) was incorrect, is that nothing is easier than to let heat down at once from the hot body to the cold, without the performance of any work. If the hot body be put into direct communication with the cold body, the same quantity of heat might be allowed to go down from one to the other, and yet give no work at all. Before we give the correct statement of the question here involved it may be well to complete this brief account of Carnot's contributions to the problem. For even with his false assumption he obtained much more than has yet been stated. We have yet to show *why* he introduced the notion of reversibility. And this is virtually what he said:—If an engine be reversible (as this cycle of operations has been

shown to be), it does as much work as can be got from a given quantity of heat under the same given circumstances. So that,—no matter what be the substance which is expanding and contracting, if a certain quantity of heat be let down from a source at a certain temperature through a reversible engine to a sink at another definite temperature, then the quantity of useful work which can be got from that heat will be absolutely the same.

Reversibility is thus the sole necessary condition of equivalence between two heat-engines.

This is an enormous step in physical science. The reasoning is independent altogether of the properties of any particular substance. Whether steam, or air, or ether, &c., be the working substance, there is the same crucial test of the perfection of an engine. That test is, *if a heat-engine be reversible it is perfect*,—perfect not in the popular sense, but in a scientific sense; that is to say, *it is as good as it is possible physically to make it.*

92. Carnot demonstrates this property by a simple *reductio ad absurdum* exactly analogous to that of § 20. He says that a reversible heat-engine is a perfect one; for, if not, suppose there could be one more perfect, and let these two engines be employed in conjunction. Let the more perfect engine be employed in taking a quantity of heat, conveying it to the condenser from the boiler, and giving from it a larger quantity of work than the reversible engine could do. Part only of the work thus gained will be required to enable the reversible engine to pump the same amount of heat back again. Every time the heat goes down, it is through the more perfect engine; every time it comes up, it is through the less perfect engine, and therefore the double system necessarily gains more work than it spends. Thus we have an engine which will not merely go for ever,

but which will for ever, without any drain on its sources, steadily do work on external bodies.

Such a consequence, as we have seen (§ 20), is inconsistent with all experimental results, and therefore the supposition which led to it, viz.—that there can be a more perfect engine than a reversible one,—is necessarily false.

Such is Carnot's proof that (on the assumption that heat is matter) a reversible heat-engine is a perfect engine. It requires very little indeed, as a moment's reflection shows, to make this reasoning consistent with modern knowledge of heat.

93. We have now to consider the cycle in the light of the conservation of energy; so that, if work be produced from heat at all, some of that heat must have disappeared in its production. Therefore, under no circumstances—if the engine be doing external work at all—can the quantity of heat which reaches the condenser ever be equal to that which leaves the boiler. If no heat has been wasted by conduction or in other unprofitable ways,—the difference between the quantity which leaves the source and the quantity which reaches the condenser during a complete cycle must be precisely the equivalent of the external work which has been done. Taking that into account, suppose we could make an engine more perfect than a reversible one. Work the two together, as before. Make the reversible engine continually restore to the source as much as the other takes from it. Then, as it is less perfect, it will require less work to be employed on it, when reversed (to restore to the source or boiler that quantity of heat), than is furnished by the other engine; and therefore, on the whole, while there is a pumping up of heat and letting it down which exactly compensate one another, at least so far as the source is concerned, there is a gain of work. But a heat-

engine, however complex, can only work by expenditure of heat—so that, as the arrangement in question takes no heat from the boiler, it must obtain it from the *Condenser*. The result amounts to this, that by taking, as the condenser for a compound engine such as that supposed, any limited portion of the available universe, the engine would continue to give out work till it had removed all heat from that portion. It may safely be assumed as axiomatic that this cannot be done; all experimental facts are against it. Thus we have it, *ex absurdo*, that there can be no engine more perfect than a reversible one. This question will be more carefully considered in a later chapter.

94. Since all reversible engines are perfect, they are all of equal efficiency: that is, they all give precisely the same amount of work from the same quantity of heat, under the same conditions. It follows that these conditions alone determine how much work can be produced, by a perfect engine, from a given quantity of heat. Now, the temperatures of the boiler and condenser are the only particulars in which this set of perfect engines agree. Suppose each to be worked till it has employed a given quantity of heat, then each would do the same amount of work. That is to say, All perfect heat-engines under the same conditions convert into work the same fraction of the heat used, and the value of this fraction depends only upon the temperatures employed. Hence follows immediately Thomson's *absolute* method of measuring temperature. (Refer again to § 82.) For it is obvious that the relation between the temperatures of the boiler and the condenser can now be defined in terms of the fraction just spoken of.

95. The terms of the definition are to a certain extent at our option. That which was finally fixed on by Thomson was chosen so as to make as near an agreement as possible

between the new scale and that of the ordinary air-thermometer, and therefore to make the introduction of this method, the only scientific one, produce as small a dislocation of previous conventions as possible. The full reasons for this particular choice will be afterwards explained. Meanwhile we simply state the definition in Thomson's words :—

The temperatures of two bodies are proportional to the quantities of heat respectively taken in and given out in localities at one temperature and at the other, respectively, by a material system subjected to a complete cycle of perfectly reversible thermo-dynamic operations, and not allowed to part with or take in heat at any other temperature: or, the absolute values of two temperatures are to one another in the proportion of the heat taken in to the heat rejected in a perfect thermo-dynamic engine, working with a source and refrigerator at the higher and lower of the temperatures respectively." [*]

96. Suppose we keep a body at the temperature of boiling water, under the condition that the barometer shall be at a height of 30 inches. (See foot-note to § 61.) Suppose we keep another body at the temperature of melting ice, with the barometer at the same height. Suppose we could measure what amount of heat is taken in, and what amount given out, by a perfect engine working between these two temperatures; these amounts of heat, as will be shown later, would be found nearly in the proportion of 374 to 274. These particular numbers have been chosen for the terms of the ratio because their difference is 100. In the ordinary centigrade scale we call the freezing temperature zero, and we call the temperature of boiling water, under the 30 inches of pressure of the atmosphere, 100°. Thus, as we see by the experiment, in the case above mentioned, that

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[*] *Trans. R. S. E.*, May 1854.

for 374 taken in, 274 are given out, the temperature of boiling water will on this scale be represented by 374°, and that of freezing water or melting ice by 274°, the range between these being the ordinary 100° of the centigrade thermometer. Hence the curious and very important result, that a body cooled down 274 centigrade degrees below zero is absolutely deprived of heat. This limit, which is commonly called the absolute zero of temperature, is perhaps more correctly called the zero of absolute temperature. And it is obvious that the temperature of a body could not be reduced so as to be lower than this.

97. The student is recommended fully to master the brief statement we have now given: for he will then be much better able to understand the relations of the various parts of our great subject than he would have been without such knowledge; and he will also understand why, in the more detailed study of them which follows, it is constantly necessary to anticipate, by borrowing materials from a later chapter.

98. *Résumé of* §§ 41—97.—Temperature is a mere condition of a body as regards Heat. The utmost fraction of a given quantity of Heat which can be converted into useful work depends solely on the temperature of the body with which it is associated, and upon the lowest temperature available. Carnot's inestimable services to science consist in his suggestion of *Cycles;* and especially of *Reversible Cycles,* for the criterion of a perfect engine. *Second Law of Thermodynamics,* and Absolute measurement of Temperature.

CHAPTER V.

DILATATION OF SOLIDS.

99. Taking the process explained in § 61 as a mode of defining temperatures between 0° and 100° of the Centigrade scale, we proceed to determine the dilatation of various bodies when they are raised to various temperatures *within that range.* One most important result of this inquiry will be found to be the (approximate) measurement of temperatures by means of these dilatations, so that we shall be enabled to get rid of the theoretically very simple but practically very cumbrous process which we first adopted for defining temperature.

The order of simplicity of *result* would lead us to commence with gases such as air and its constituents, but as we cannot experiment on them except when they are enclosed in solid vessels, simplicity of *process* requires that we commence with SOLIDS.

The importance of this inquiry from the merely popular point of view consists mainly in the common applications of the results to such matters as the regulation of watches and clocks, and the correction of measuring-rods for changes of temperature. Its pure scientific interest is of a far higher order.

100. A Solid which has the same properties at all points is called *homogeneous*, otherwise it is *heterogeneous.* But even a homogeneous solid has not necessarily the same properties

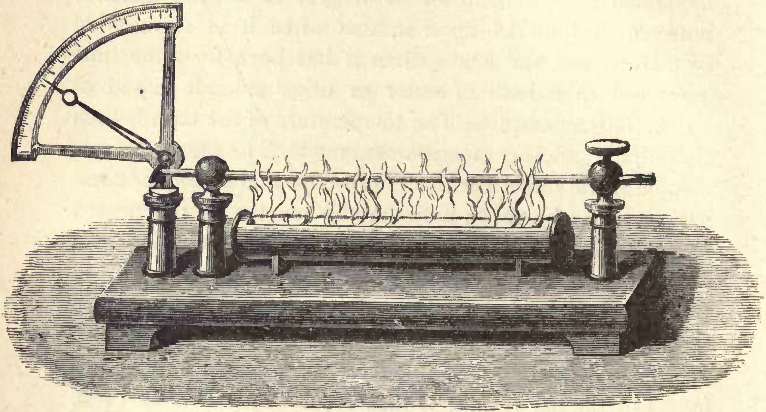
in all direotions. The grain of wood, of fibrous iron, the crystalline forms and cleavage planes of minerals, the planes of deposition and of cleavage in slates and sandstone rocks, and many analogous phenomena, familiarize us with the idea of solids which are homogeneous but not *isotropic.* An isotropic body, then, is one from which if a small sphere were cut, it would be impossible to tell by any operation on it how it originally lay in the solid—it has, in fact, precisely the same properties in all directions. Probably there does not exist any solid absolutely isotropic as regards all its physical properties, but such substances as non-crystalline metals (lead, gold, silver, copper,) and well-annealed glass may be taken as approximately isotropic as well as homogeneous. We commence our work with a rod or bar of such a material, and we define thus:—

The *co-efficient of linear dilatation* at any temperature is the ratio which the increment of length of the bar when its temperature is raised one degree bears to the original length.

101. As the bar is supposed to be homogeneous, and to be raised to the same temperature throughout, each inch of its length increases by the same amount; so that the whole increase of length is directly proportional to the original length. To obtain a result independent of the dimensions of the specimen chosen, we must therefore take the *ratio* of the increase to the whole original length:—which is the statement made in the definition. The linear dilatation might be put in the more formal terms of a *specific* property of the substance, by operating on a bar of unit length, and then defining its increase of length for one degree of temperature as the dilatation required. But, practically, no one operates on an exact unit, and therefore we must make our definition such as to be independent of the length of the specimen operated on; and of course independent of the standard of length.

102. As this work is not designed to teach the details of experimental *methods*, which are in all cases much more readily and also more appropriately taught in the laboratory than in the lecture-room or by books, it is sufficient to say that the co-efficient of dilatation of a bar is usually obtained by actual measurement of its length, or of the distance between two marks upon it, first when it is surrounded by melting ice, and again when it has been for some time immersed in a bath of water or other suitable liquid at a definite temperature. The temperature of the bath is then altered, and another measurement made. The measurements may be made directly with a microscope and screw, or comparisons may be made between the lengths of the heated bar and of another kept permanently in melting ice in a second bath placed alongside of the first. Methods in which one end of the bar is clamped, while the other in expanding moves a bent lever or a mirror, are not so trustworthy as those in which the distance between two known points of the bar is directly measured. Their principal use, and it is often a very important one, is in lecture illustrations. The principle on which they depend is very simple.

One end of the bar or rod is clamped in a pillar A; the other end, passing freely through a hole in the pillar B, presses against the back of a plane mirror supported on a horizontal axis at C, perpendicular to the rod. (The reader may easily supply the diagram for himself.) Any advance of the free end of the rod must of course be due to expansion, and its amount can be at once determined by the change of direction of a ray of light reflected from the mirror, for that change is double the angle through which the mirror rotates. And the tangent of the angle through which the mirror rotates is the ratio of the increase of length of the bar to the height of the axis C above it. Thus by lowering C the sensibility of the arrangement admits of almost unlimited increase. The annexed cut represents the old form of this arrangement, where a bent lever is used instead of the mirror.



A method of extreme delicacy has recently been introduced by Fizeau. It depends upon what are called Newton's rings, an optical phenomenon caused by the retardation of light in passing twice through the air-space between a lens and a flat plate of glass. The colour produced varies with the distance of the plate from the lens:—so that if one be fixed, and the other carried on the end of an expanding rod, the changes of colour enable us to measure with great accuracy the expansion of the rod.

103. The general result of such measurements is found to be the very simplest possible :—

The ratio of the increase of length to the length at zero is proportional to the rise of temperature.

Let l_t represent the length of an assigned portion of the bar at temperature t°C, then the above experimental result is at once stated in the form

$$\frac{l_t - l_0}{l_0} = kt \quad . \quad . \quad . \quad . \quad . \quad (a)$$

where k is the coefficient of proportionality. Hence, if we put $t = 1$, we see by the definition (§ 100) that k is the *coefficient of linear dilatation* at zero.

The value of k is usually so small that to determine it with any accuracy we must use a considerable change of temperature. Taking then the extreme temperatures of our temporary scale—*i.e.* measuring the length of the same bar, first in melting ice and then in boiling water—we have

$$\frac{l_{100} - l_0}{l_0} = 100\,k.$$

The coefficient of linear dilatation is therefore the one-hundredth part of the ratio which the increase of length of the bar between the temperatures 0°C and 100°C bears to the length at 0°C.

104. It is rarely found that two specimens even of the same material possess any one specific property to *exactly* the same amount. This remark applies even to natural crystals, much more therefore to artificial substances such as glass, &c., so that it is impossible to give any perfectly definite general statements of Dilatation-Coefficients. The following numbers must therefore be taken merely as an illustration of the sort of results arrived at; quite sufficient as a basis for some general remarks upon the subject, but altogether unfit for any application in delicate calculations or constructions. When an optician (worthy of the name) has discs of flint and crown glass supplied him for the

purpose of making an achromatic lens, he does not look up tables of results of former experimenters to find the refractive index, he has to measure with great care for himself this particular constant for the material of each of the discs, and for more than one definite wave-length of light. The constructor of really high-class electrical apparatus, be it the smallest galvanometer or the longest submarine cable, most carefully chooses his copper by a determination of its specific resistance. And similar statements are, or ought to be, true in every practical branch of physical science.

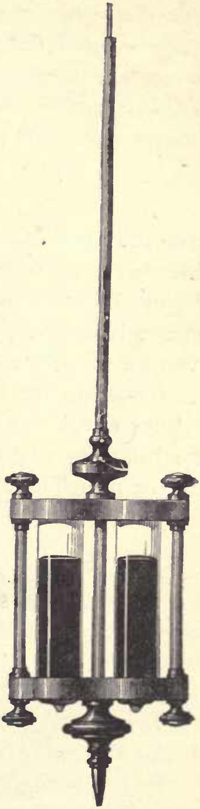
APPROXIMATE COEFFICIENTS OF LINEAR DILATATION OF ISOTROPIC SUBSTANCES.

Glass	·0000085	=	$\frac{1}{120,000}$
Platinum	·0000085	=	$\frac{1}{120,000}$
Steel	·0000121	=	$\frac{1}{85,000}$
Copper	·0000191	=	$\frac{1}{52,000}$
Zinc	·000029	=	$\frac{1}{34,000}$

105. The foregoing table, meagre as it purposely has been made, shows two marked results. *First*, the Coefficient of Linear Dilatation is in general very small; *secondly*, its values are very considerably different in different solids.

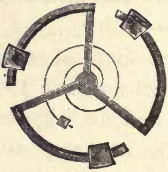
From the first result it follows that, unless very delicate operations or very high temperatures are involved, temperature-change of dimensions in solids may be neglected except when we are dealing with great lengths such as the iron girders of a bridge, or the rails on a railway.

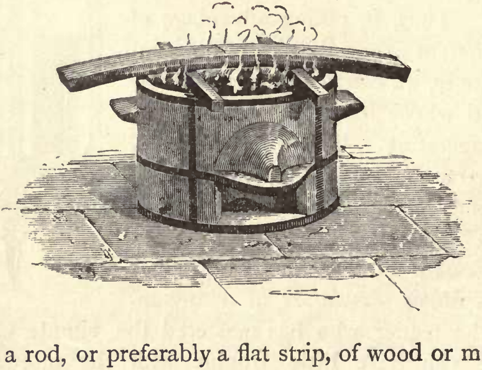
From the second result, coupled with the experimental law of § 103, it appears that we may by means of combinations of two different materials produce *compensation*, if we arrange so that the distance between two assigned points of a complex system shall be increased by the expansion of some of its parts, and diminished to an equal amount by the expansion of others.



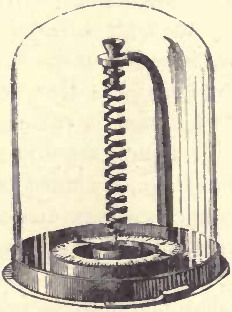
Thus, to take the simplest conceivable arrangement, let us have two similar bars, of zinc and of copper, placed parallel to one another, and fastened at one end to a transverse piece. The condition that the distance between two uprights, fixed to the free ends of these bars, shall remain constant at all ordinary temperatures is simply that the *actual* expansion shall be the same for each bar. But, as the Coefficients for zinc and copper are to one another as 29 to 19, this will be at once secured by making the *lengths* of the bars as 19 to 29. Thus, by taking advantage of the different expansibilities of different substances, we can construct a measuring-rod whose length is independent of temperature. This is, practically, the same arrangement as that of Graham's mercurial *Compensation Pendulum.* A slightly more complex arrangement of the same kind gives the *Gridiron Pendulum* of Harrison. But the reader who has mastered the simple case given above can have little trouble with the more complex cases.

106. The balance-wheel and its spring perform for a watch or chronometer precisely the same function as the pendulum, assisted by gravity, performs for a clock. But here the application of the compensation process is considerably more complicated, because gravity is constant in the clock, while the coefficient of elasticity of the chronometer balance-spring depends on its temperature. However, we may for the present consider only the question of compensating for the increased moment of inertia of the balance-wheel due to expansion. [The effect of heat on the balance-spring usually renders *over*-correction necessary, but the principle is the same.]





When a rod, or preferably a flat strip, of wood or metal is bent it is known that the layers on the convex side are extended, those on the concave side compressed, relatively to the intermediate ones. Hence it is obvious that such a strip *would bend itself* if the layers on one side of its mesial plane were to be extended or contracted relatively to those on the other. Thus a strip formed by soldering or brazing together strips of two metals of different expansibilities will become curved by change of temperature, the more expansible metal being on the convex side when the whole is heated, and on the concave when it is cooled.



Now suppose the rim of the balance-wheel to be constructed of two concentric layers, the outer the more expansible. Also let it be cut into separate arcs sufficiently removed from one another to prevent interference. Then it is easy to see that the expansion of the radial bar tends to increase the moment of inertia of the whole, while the increased curvature of the arc tends to diminish it. A ribbon of two differently expansible metals similar to that just described was employed by Bréguet for the purpose of constructing an exceedingly delicate thermometer. The ribbon was usually coiled into a helix which was fixed vertically in a support at its upper end, while the lower end carried a light index travelling on a horizontal dial. The ribbon is so thin that it almost instantly acquires the same temperature as the surrounding medium, and its capacity for heat is so small that it does so without sensibly affecting the temperature of the medium.

107. One fact of exceeding great use in practice appears in the short table of § 104. The coefficient is nearly the same for platinum as for glass, and farther experiment shows that this is at least approximately true for a very wide range of temperature. In consequence of this a platinum wire may be "*fused in*" to a glass vessel:—the glass, melted under the blow-pipe, adhering to the hot wire, and the two materials contracting equally as they are allowed gradually to cool, so that the junction is perfectly air-tight. If the attempt be made with a wire of gold or of any other metal whose melting-point is high, it almost certainly fails however thin be the wire:—either the glass cracks on cooling; or the wire contracts more than the glass, so that the junction is not air-tight.

108. The facts that platinum is practically infusible in any ordinary furnace, and that its coefficient of linear dilatation changes very little through great ranges of temperature, have led to its employment for the rough measurement of high temperatures. Instruments of this rude kind are usually called *Pyrometers.* The principle on which they work is to keep a record of the length which a bar of platinum had while plunged in the furnace, so that it may be compared accurately with the length of the bar when cold.

The bar is put into a hole bored in a piece of graphite or plumbago, whose dilatation is exceedingly small. The bar rests against the bottom of the hole and is kept there by a tightly-slipping plug of graphite or baked clay. As the platinum expands by heat it pushes this plug forward, but when it cools it does not draw it back. The principle is exactly that with which every one is familiar in the ordinary maximum thermometer.

109. When a body is *aeolotropic*, *i.e.*, non-isotropic, its properties are not the same in all directions. But, though the circumstances are now less simple than in the case of isotropic bodies, they are usually by no means very complex. For in general, even in the most complex cases, these properties can be referred to three definite directions at right angles to one another. When these directions are ascertained, and measurements of a particular property (as of coefficients of linear dilatation, with which we are at present engaged) are made parallel to them, the value of the property for any other assigned direction may be calculated by a simple process.

[It would require a little more of mathematical reasoning than can well be introduced into an elementary work to show that, whereas the properties of an isotropic body are analogous to those of a sphere, those of an aeolotropic body have the same relation to an ellipsoid. This and what follows we take for granted. An ellipsoid may be regarded as formed from a sphere, by selecting three diameters at right angles to one another, and extending or compressing the whole sphere to different amounts in directions parallel to these three lines. An ellipsoid is known if the directions and lengths of its three principal axes (which are the three lines at right angles to one another) are known. When the lengths of any two of its axes are equal it becomes an ellipsoid of revolution (*prolate* if the third axis is the longer, *oblate* if it is the shorter, of the three); and when all three are equal it becomes a sphere. Thus when the amounts of compression or extension parallel to *two* of the three diameters are equal, the sphere becomes an ellipsoid of revolution; when all three amounts are equal, it remains a sphere. Every plane section of an ellipsoid is an ellipse. Every ellipse which has equal conjugate diameters in directions perpendicular to one another is a circle. An ellipsoid which has two plane circular sections such that the line joining their centres is perpendicular to their planes is an ellipsoid of revolution, of which the line just mentioned is the axis. All lines through the centre of an ellipsoid of revolution, and equally inclined to the axis, are equal. If it have been formed from a sphere by one elongation and two equal contractions, or by one contraction and two equal elongations, there will be a set of diameters (all equally inclined to the axis) which are each unaltered in length.]

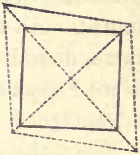
110. By far the most homogeneous substances we possess are natural crystals. None are absolutely isotropic, for all have planes of more or less perfect cleavage. But one great class of crystals, those of the *first* or regular system (with a few curious exceptions, probably only *apparent*), are isotropic as regards light, and are also isotropic as regards heat. Substances so very different as diamond, galena, rock-salt, &c., belong to this system, and their coefficients of linear dilatation are the same in all directions.

Crystals of the prismatic and rhombohedral systems, and in general bodies which have *one* optic axis as well as one axis of crystalline symmetry, have their greater or lesser coefficient of linear dilatation in the direction of that axis, and are equally expansible in all directions at right angles to that.

All other crystalline bodies have three principal dilatation-coefficients, different from one another, and in directions at right angles to one another.

111. Optical instruments, such as the reflecting goniometer, enable us to measure with very great accuracy the angles between the plane faces of crystals; and measurements of angle are in general much more exact and useful for such inquiries as those in which we are now engaged than direct measures of length. It was, in fact, almost entirely by measurements of angles that Mitscherlich and others arrived at the results briefly stated in § 110.

As a simple illustration, suppose a square prism to be cut from an aeolotropic body, so that the diagonals of one of its ends are parallel to any two of the chief axes, and have in general different coefficients of linear dilatation. An application of heat will necessarily change the square into a rhombus as in the cut, and the ratio of the lengths of the diagonals is very accurately found by measurement of one of the angles.



The defect of this method is that it gives the *difference* of the linear dilatations in the directions of the two diagonals, but not the actual amount of either. For if the diagonals were of unit length at 0° C, their lengths will be $1 + k_1t$ and $1 + k_2t$ at t° C, and the tangent of half the measured angle of the rhombus is

$$\frac{1 + k_2t}{1 + k_1t}, \text{ which is practically } 1 + (k_2 - k_1)t,$$

because k_1 and k_2 are both exceedingly small.

Suppose two such prisms cemented together as below,

the edges brought into contact being those whose angle becomes more obtuse by heating. The upper surface will form a continuous plane mirror when the whole is cool, but will consist of two inclined mirrors after heating. An almost infinitesimal difference of expansibility in different directions can be detected by observing with a small telescope the image of a distant object formed by reflection at the surfaces of the prisms.

What are called twin-crystals are made up of two parts put together in a manner somewhat similar to that just described: and the phenomena are beautifully seen when a polished slab of "arrow-headed" selenite is slightly warmed.

112. By the optical method the differences between the principal dilatation coefficients are very accurately determined. All that remains to be done is to measure *one* of them directly, by the methods already referred to (§ 102). Here Fizeau's method, already described, may be used with advantage.

When this is done it is found that in some bodies, notably in Iceland spar, the difference of two dilatation coefficients is greater than either. In other words this substance, which has *one* axis of symmetry, expands parallel to its axis when heated, but simultaneously *contracts* equally in all directions perpendicular to the axis.

It follows from the explanation in § 109 that there are an infinite number of directions, equally inclined to the axis, in which Iceland spar neither expands nor contracts. As a similar property is found in certain masses of marble, Brewster long ago suggested the use of a cylinder of this substance, cut in a proper direction, as an invariable pendulum.

But the apparent anomaly of contraction by heating is not confined to crystalline bodies. We shall presently have to discuss it as shown by water, but a very instructive instance is furnished by india-rubber.

If the spiral wire be extracted from an ordinary vulcanised india-rubber gas-pipe, and the pipe be then suspended vertically, *with a weight attached to its lower end*, it contracts (in some specimens by five or even ten per cent. of its length) and raises the weight, when steam is blown through it from a little boiler. Thus we have a contraction, easily visible to a large audience, without any of the artificial processes alluded to in § 102 for the exhibition of expansion.

113. The experimental result of § 103 involves, as a consequence, the farther statement:—

The coefficient of cubical dilatation is in all cases the sum of the three chief coefficients of linear dilatation.

This is easily seen by supposing a body to be divided into a number of brick-shaped portions, with their edges parallel to the three chief axes. The lengths of the several edges of each brick are increased by heating from 0° to t° C in the ratios

$$1 : 1 + k_1 t, \quad 1 : 1 + k_2 t, \quad 1 : 1 + k_3 t,$$

and thus we have for the final, in terms of the original, volume

$$V_t = V_o (1 + k_1 t)(1 + k_2 t)(1 + k_3 t),$$

or, what comes to the same thing, since the quantities k are always exceedingly small

$$\frac{V_t - V_o}{V_o} = (k_1 + k_2 + k_3)t.$$

This is precisely the same formula as (a) of § 103, and thus the above statement is verified.

When the body is isotropic the values of k are equal, and the coefficient of cubical dilatation is *three times* that of linear dilatation. Thus, for such bodies, only one determination (whichever may be the easier, or the more exact) need be made.

In aeolotropic bodies there may be expansion, contraction, or no change of volume, as a result of rise of temperature.

Thus, just as there may be change of volume without change of form, we may have change of form without change of volume.

114. Most of the modes of directly measuring change of volume depend on the use of expansible liquids. Hence, in describing their principle, we shall suppose first a non-expansible vessel and a non-expansible liquid, and then show how to correct for the expansion of the vessel; leaving to a later section to show how the expansion of any actual liquid may be measured and allowed for.

Let a vessel containing the solid whose cubical dilatation is to be measured be filled up to the end of its (narrow) neck with an inexpansible liquid, and let the whole be weighed. Then let it be raised to a known temperature, the expansion (if any) of the solid will drive out some of the liquid. Let it cool, and weigh it again. The difference of weight is the weight of the liquid driven out by the expansion of the solid.

The correction for the expansion of the vessel, the material of which is usually glass or some other isotropic substance, is, by § 113,

$$V_t - V_o = 3k V_o t,$$

where k is its coefficient of linear dilatation.

115. The greater part of what precedes is only approximately true, even for the small range of temperature (0° to 100° C.) to which our statements have been, in the main, confined.

Measurements carried out at much higher temperatures have shown that the coefficients both of linear and of cubical dilatation are not constant, but increase slowly with rise of temperature. We are not aware of any experiments made with the view of deciding whether, as is probable, these coefficients become gradually less as the temperature is lowered below zero.

It has been tacitly assumed, in what precedes, that heating has not permanently altered the molecular state of the solid operated on. So long as this is the case the dimensions of the body are always practically the same at the same temperature, whether the body is being heated or is cooling. But it is familiar to every one that sudden cooling has often a marked effect on the properties of a body. The process of "annealing," as it is called, is devised essentially for the purpose of preventing such physical changes. The whole of this subject, with the exception of a few rules discovered tentatively, is still very obscure. Think, for instance, of the very different conditions of stress, &c., under which the different parts of a Rupert's drop are successively solidified. A recent great practical improvement in the manufacture of steel depends essentially upon causing it to solidify under considerable pressure.

116. *Résumé* of §§ 99—115.—The linear dilatation of a solid rod is approximately proportional to the rise of temperature. Hence, in isotropic solids, the cubical dilatation (being threefold the linear dilatation) is also proportional to the rise of temperature. Special exceptions, in the case of aeolotropic bodies. Applications to measuring-rods, compensation balances and pendulums, pyrometers, Bréguet's metallic thermometers. Irregularities due to rapid cooling, &c.

CHAPTER VI.

DILATATION OF LIQUIDS AND GASES.

117. In fluids this question is much more simple than in solids, for we have cubical dilatation only. Taking liquids first, we find that in general their cubical dilatation is, like that of solids, proportional directly to the rise of temperature, but greater.

Exceptionally great labour and experimental skill have been devoted to this point, in the case especially of two common liquids:—*mercury*, because of its importance in thermometers; and *water*, because its expansion at ordinary ranges of temperature is anomalous, and because this anomaly is closely concerned with the laws of its circulation. We propose to devote several sections to each of these liquids, as they may be considered typical.

Meanwhile we may merely remark that what we seek is the real dilatation; not what is called *apparent* dilatation, which is affected by the dilatation of the vessel.

118. Let, as in § 114, a glass vessel with a very narrow neck be weighed when full of mercury at 0° C; then let it be heated to t° C, and weighed again after cooling. Let these weights be W_0, W_t, respectively, and let w be the weight of the empty vessel.

Then, as the vessel at 0° holds an amount of mercury whose weight is

$$W_0 - w,$$

it would hold at temperature t° an amount whose weight is

$$(1 + 3kt)(W_0 - w),$$

provided mercury were not expansible. It actually holds an amount whose weight is only $W_t - w$. The ratio of these two numbers is therefore that of the densities of mercury at 0° and at t°; and, if K be the mean coefficient of cubical dilatation of mercury between 0° and t°, we have

$$(1 + Kt)(W_t - w) = (1 + 3kt)(W_0 - w),$$

from which K may at once be calculated.

To verify this equation, suppose the cubical dilatation of the liquid to be the same as that of the vessel, *i.e.*

$$K = 3k,$$

then we have at once

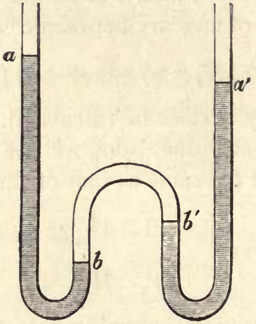
$$W_t = W_0,$$

showing that the vessel remains just filled at all temperatures.

119. This process is a simple and effective one, although it involves the determination of the expansion of the vessel as well as of the liquid; and it is so because the expansion of mercury is much greater than that of glass. But a very ingenious method of determining the expansion of a liquid, independently of that of the solid in which it is enclosed, was devised by Dulong and Petit, and applied with great skill by Regnault. The principle of the method is merely that of the simple hydrostatic equilibrium of two liquids, one in each of the branches of a U tube: viz., that the heights of the separate columns above the common surface

(where the liquids meet) are inversely as their specific gravities.

In practice, to avoid direct contact between the hot and cold liquids, an air-space is made to intervene, so that the essential parts of the arrangement are as in the sketch. The tube is now a double U, one half of it being surrounded by a vessel containing ice-cold water, the other by a vessel whose liquid contents may be raised to any desired temperature.



The columns *a b*, *a′ b′*, of mercury are each exposed to the pressure of the atmosphere at their upper ends, and at their lower ends to the pressure of the air in *b b′*. Hence, if the differences of level of the surfaces at *a* and *b*, and at *a′* and *b′*, be measured with a cathetometer, the mercury in each tube has a density inversely as the corresponding measured number.

120. Here are a few of Regnault's numbers for mercury:—The second column contains numbers derived directly from the experiment described; the third is calculated from the second for a special purpose:—

DILATATION OF MERCURY.

Temperature C.	Mean coefficient of dilatation from 0°.	Coefficient referred to vol. at 0°.	True Coefficient.
0°	—	0·0001791	0·000179
50	0·0001803	0·0001815	0·000180
100	0·0001815	0·0001841	0·000181
150	0·0001828	0·0001866	0·000182
200	0·0001840	0·0001891	0·000183
250	0·0001853	0·0001916	0·000184
300	0·0001866	0·0001941	0·000185
350	0·0001878	0·0001967	0·000186

We have extended the list to temperatures far higher than those already temporarily defined, in fact up to the boiling point of mercury. As given in the table they are measured by the air-thermometer presently to be described.

Meanwhile the numbers above give, as the reader may easily verify, the following very simple formula for the usually employed coefficient of cubical dilatation of mercury at any temperature $t^\circ C$:—

$$K_t = 0{\cdot}0001791 + 0{\cdot}00000005t.$$

Thus if t be 250:—

$$K_{250} = 0{\cdot}0001791 + 0{\cdot}0000125 = 0{\cdot}0001916,$$

as given in the table. As this formula agrees with all the given numbers, it may safely be employed to calculate K for any intermediate temperature.

It will be observed that the coefficient of dilatation increases steadily with rise of temperature. This is found to be the case with the great majority of liquids, through the whole range of temperature in which we can experiment upon them. But the rate of increase of the coefficient is generally greater as the temperature of the liquid rises towards its boiling point.

The last column in the table gives the *true* coefficient of dilatation—being (according to the analogy of the definition in § 100) the ratio which the increment of volume for one degree of rise of temperature bears to the *original* volume:—not (as is tabulated in the third column in accordance with common usage) to the volume at zero C. With solids, in general, the dilatation is so small that this distinction is of little importance—but a comparison of the two last columns just given, shows that it cannot be neglected for a liquid like mercury. The formula for this true coefficient is very nearly

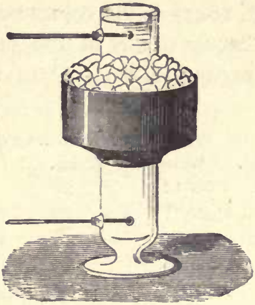
$$K_t = 0{\cdot}0001791 + 0{\cdot}00000002t.$$

In this case, and in that of water which follows, we abandon for a time the rule laid down in § 104, and enter into details. The reason is that we are now dealing with a *perfectly definite* substance, whose properties (under the same conditions, § 9) are the same at all times and in all places;—not a substance like glass or brass, &c., of which different specimens may differ seriously from one another.

121. The behaviour of water between 0° and 100° C is very different from that of mercury. From 0° upwards it contracts, more and more slowly, till it reaches its *maximum density* almost exactly at 4° C. From 4° upwards it expands, at first very slowly, then faster and faster to 100°.

The usual class-illustration of this phenomenon is known as Hope's experiment. It depends on the simple hydrostatic law that, when a heterogeneous fluid is in stable equilibrium under the action of gravity, the density increases from above downwards.

Hope merely applied what is called a freezing mixture (a mixture of common salt with snow or pounded ice is quite sufficient) to the middle of a cylindrical jar full of water. Thermometers were fixed by corks in holes in the side of the jar, so as to indicate the temperatures of the upper and lower stratum of water.



Before the freezing mixture is applied, provided the temperature of the water is above 4° C, there is usually a slight excess of temperature indicated by the upper thermometer—showing that the warmer water is less dense than the colder. The first effect of the freezing mixture is to reduce the temperature shown by the lower thermometer, without perceptibly affecting the higher. This goes on till the lower thermometer reaches 4° C, for then it ceases to descend; very soon afterwards the temperature indicated by the higher thermometer begins to sink in its turn. *But it does not stop at* 4° *C*. It shows lower and lower temperatures till the water towards the top of the vessel begins to freeze, and is therefore at 0°. Thus water at 4° C is proved to be denser than at any other temperature from 0° to 100°, because it remains persistently at the bottom of the vessel whatever be the temperature of the water above it.

Such an experiment, however, is not adapted for the measurement of coefficients of dilatation. Some experimenters have for this purpose weighed a lump of glass in water at different temperatures, others have operated by the process indicated in § 119. The following are from Kopp's paper (*Poggendorff*, 1847):—the volume of water at 4° being taken as unit, the excess of any of the other numbers over unit is the whole expansion from 4° to the corresponding temperature:—

Dilatation of Water at Ordinary Pressure.

Temp. C.	Vol. of Water.	Temp. C.	Vol. of Water.
0°	1·00012	20°	1·00169
2	1·00003	30	1·00420
3	1·00001	40	1·00766
4	1·00000	50	1·01189
5	1·00001	60	1·01672
6	1·00003	70	1·02237
8	1·00011	80	1·02871
10	1·00025	90	1·03553
15	1·00082	100	1·04312

The numbers in this table, from 0° to 20°, are represented with a fair degree of approximation by the formula

$$V_t = 1 + \frac{(t-4)^2}{144{,}000}.$$

Hence the coefficient of dilatation of water (between these limits) is approximately

$$K_t = \frac{t-4}{72{,}000}.$$

Matthiessen, Pierre, and Hagen have given experimental results, the mean of which tends to show that the denominator of this fraction should be more nearly 68,000.

According to Despretz, the volume of water when cooled more than four degrees below its temperature of maximum density increases somewhat faster than if the water be heated to the same number of degrees above that point. Water can be cooled several degrees below 0° C without freezing, provided it be not agitated.

It was found by Canton, in 1764, that the compressibility of water is greater in winter than in summer. It follows from this that, as will be shown later, *the maximum density point is lowered by increase of pressure.* The experimental data do not yet enable us to obtain very definite information, but we may say (roughly) that a pressure of 50 atmospheres lowers the maximum density point by 1° C. The freezing point also is lowered, but not so much.

122. The most expansible of all known liquids are those which require considerable pressure to keep them in the liquid state. The coefficients of dilatation of sulphurous acid, or carbonic acid, in hermetically sealed tubes, are considerably greater than that of air.

The following are some of Thilorier's results for the density of liquid carbonic acid in presence of its vapour at different temperatures:—

Temperature.	Density.
— 20 C.	0·90
0 C.	0·83
+ 30 C.	0·60.

Thus the mean expansion for 1° between 0° C and 30° C is 0·013 nearly.

As a rough general rule it may be stated that (at ordinary temperatures) the more volatile a liquid is the greater is its co-efficient of dilatation. Alcohol, however, (whose co-efficient of dilatation is 0·00105 at 0° C.) is considerably more expansible than ether.

123. When we come to consider the expansion of gases, we find a problem quite different from those we have already treated. For a given quantity of a gas cannot be said to have any particular volume, unless we specify the vessel in which it is confined, or the pressure to which it is subjected. The effects of moderate pressures upon the volumes of

solids and of the majority of liquids are so small that we have not found it necessary to take them into account while discussing the expansion of such substances. In fact a solid or a liquid will expand very much as we have already described, even if it be confined in an envelop of considerable strength—simply bursting the envelop if it does not otherwise yield. But, practically, no superior limit has yet been assigned to the volume which a given quantity of air will occupy at ordinary temperatures; and on the other hand a strong vessel containing a gas at atmospheric pressure would be melted or at least softened before the contained gas had been raised to a sufficient pressure to burst it.

It follows, then, that we must measure either the dilatation (*i.e.* ratio of increase of volume to original volume) of a gas kept at a constant pressure; or the ratio of increase of pressure to original pressure, in a gas kept at constant volume; each for a given rise of temperature.

The first rough experiments, due to Charles about 1787, and the subsequent more perfect measures of Gay Lussac, indicated that the quantities just defined are not only *the same in any one gas*, but have *the same common numerical value for all gases*, at least for the range from 0° to 100° C.

Though these results are only approximately true, they are sufficiently exact for many very important applications, both theoretical and practical, and therefore we will devote a section or two to the study of their consequences before stating the more accurate results of modern experiments.

124. In 1662 was published by the Hon. Robert Boyle the experimental fact now called

BOYLE'S LAW.

The volume of a given mass of gas, kept at a given temperature, is inversely as the pressure.

Along with this we may take (in a somewhat extended form) the result stated in last section, which is called

CHARLES' LAW.

The volume of a given mass of gas, kept at a constant pressure, increases by a definite fraction of its amount for a given rise of temperature.

The two laws together may be stated in the simple form

$$p\,v = C(1 + at),$$

where C is a constant quantity for any one gas (depending in fact upon its quantity and quality), and a is the coefficient of its cubical dilatation.

The first really good determination of the value of a was made by Rudberg. For our present purpose we may take

$$a = 0{\cdot}003665.$$

125. Three remarks must, at this stage, be made on the statement of last section.

First.—Note the remarkable fact that the coefficient of dilatation is (practically) the same for all gases. This points to a common simplicity of behaviour, and gives a hint that a gas-thermometer is probably to be preferred to a mercurial one.

Second.—Note that the two forms of statement (§§ 123, 124), which we have used in giving Charles' result, are really deducible from one another by the help of Boyle's law. This is obvious from the equation written in last section;—because p and v are similarly involved in it.

We have stated Charles' law as holding for all temperatures intermediate to 0° and 100° C. Practically this is true, though it seems to have been tacitly assumed.

Third.—If we assume the formula of § 124 to hold for *all* temperatures, we arrive at the very important result that p or v must vanish at a particular temperature, which is the same for all gases: *i.e.* if any gas be cooled to the particular temperature

$$t = -\frac{1}{\alpha} = -\frac{1}{0{\cdot}003665} = -273^\circ \textit{ nearly},$$

which makes the expression $1 + \alpha t$ vanish, then either:—it will cease to have any volume:—or *it will cease to press upon the walls of the containing vessel.* Thus we obtain a first rough hint of the position of the *absolute zero* of temperature, *i.e.* the temperature of a body altogether deprived of heat.

It may be well to recall the student's attention, in passing, to the hint (given in § 96 above) that such an absolute zero does exist, and to state that the above rough approximation gives a fairly satisfactory notion of its position on the ordinary centigrade scale. The only lawful methods, however, of treating such questions are those based upon the general laws of Thermodynamics, which apply to all bodies: and not on the properties, simple in their statement though they be, of any particular class of substances.

126. If we would shift our zero-point, which is (§ 61) wholly at our option, to the absolute zero thus determined, we must put $t - \frac{1}{\alpha}$ for t, and the expression for the laws of Boyle and Charles (§ 124) becomes

$$pv = Rt,$$

where R is a definite constant for each gas.

As already stated (§ 123) this is only approximately true, and the divergences from it will be afterwards carefully considered; but the degree of approximation is found to be closest in those gases which are least easily liquified;

and closer for any one gas the higher its temperature is raised, and (with limitations) the more it is rarefied.

The Kinetic theory of gases, presently to be described, shows us that the smaller the mutual action of the particles of a gas, when not in contact, in comparison with the action during collision, the more nearly should the above equation be satisfied. Hence we speak of the *ideal perfect gas* as a substance between whose particles there is no action except at the instants of collision—and in which therefore (as it is proved in the Kinetic theory of gases) the product of the pressure and the volume is strictly proportional to the absolute temperature.

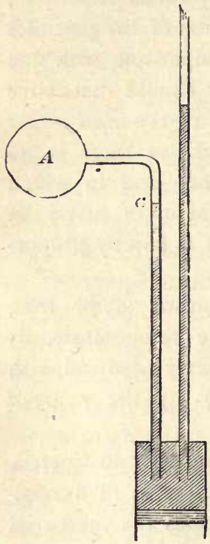
The experiments of Joule and Thomson show that, under such circumstances, the absolute temperature, as indicated by the ideal perfect gas, is strictly identical with absolute temperature as defined (§ 96) by the help of Carnot's reversible cycle.

Hence the air-thermometer, when properly constructed, furnishes a measure of temperature much more in accordance with thermodynamic theory than does the mercurial thermometer.

But it is necessary again to observe (as in § 59) that it does not at all matter what instrument is used, provided it be a good one of its kind, and *provided its indications can be translated into the corresponding absolute temperatures* as defined in § 95.

127. Recurring to the statements of § 123, we may now give an idea of the methods employed by Regnault in his classic investigations. The nature and use of the apparatus he employed are, in all the more essential features, sufficiently indicated by the rudimentary diagram on the next page, which represents a somewhat simplified form devised by Balfour Stewart.

Two vertical glass tubes, of equal bore (to get rid as far as possible of the effects of capillary forces), are fastened vertically into the lid of a closed vessel full of mercury. The capacity of this vessel can be altered at will by screwing in, or unscrewing, a plug or piston. One of the tubes is open at the top, the other terminates in a glass balloon A, containing the gas to be experimented on. This balloon, and as much of the stem as is necessary, are surrounded alternately by melting ice, and by steam from water boiling at 1 atmosphere (§ 134).



When the change of volume at constant pressure is to be measured, the plug is screwed in or withdrawn till the mercury stands at the same level in each of the tubes at each of the temperatures selected. The pressure of the gas in A is then exactly that of the atmosphere for the time being, and the volume of the gas in A and its stem must be accurately measured at each temperature. A correction (small in comparison with the change of volume of the gas) must of course be made for the dilatation of the balloon by heat.

When the change of pressure at constant volume is to be determined, the plug is adjusted at each temperature so as to bring the surface of the mercury to a definite point, *a*, on the tube carrying the balloon: and the difference of levels of the mercury in the two tubes is to be added to the column of mercury in the barometer for the estimation of the pressure of the gas. In addition to the correction for dilatation of the balloon by heat, there is also to be applied a correction (determined by experiment) for its dilatation by increase of pressure.

Other methods were employed by Regnault, such for instance as to fill with mercury, and weigh, a glass vessel with a narrow neck. Thus the capacity of the vessel is ascertained. Then, filling the vessel with dry air, to heat it to 100° C., to seal it hermetically while the contained air was thus rarefied; open it when cold under mercury, and weigh the quantity of mercury which entered. But it is sufficient to say that the results of these experiments agreed satisfactorily with those obtained by the first-described apparatus.

128. The following are a few of Regnault's results:—The first column is the ratio of the volume of the gas at 100° to that at 0° C. under atmospheric pressure; the second the pressure at 100° C. when the gas is taken at a pressure of 1 atmosphere at 0° C. and heated without change of volume:—

Hydrogen	1·3661	1·3667
Air	1·3670	1·3665
Nitrogen	1·3670	1·3668
Carbonic Oxide	1·3669	1·3667
Carbonic Acid	1·3710	1·3688
Sulphurous Acid	1·3903	1·3845

It is to be observed that, except in the case of Hydrogen, the numbers in the first column are larger than those in the second. Also that for the less easily liquifiable gases, such as the four first in the table, the numbers are all nearly equal—while for the easily liquifiable gases they differ widely, and the more so the more easily liquifiable is the gas.

129. The following numbers, also determined by Regnault, show the ratio in which the pressure is increased at constant

volume, for the same range of temperature, at initial pressures greater and less than an atmosphere :—

	Pressure in Atmospheres at 0°.	Ratio of increase of pressure from 0° to 100° C.
Air	0·1444	1·36482
	1·0000	1·36650
	4·81	1·37091
Carbonic Acid	0·998	1·36856
	4·722	1·38598

Thus, for a range of pressures from 1 to 4·8 atmospheres, the ratio for air changes by about $\frac{1}{309}$th, while in a range of but 1 to 4·7 atmospheres the ratio for carbonic acid changes by more than $\frac{1}{80}$th.

For dilatation under constant pressure, in the same range of temperature, we have—

	Pressure in Atmospheres.	Ratio of volumes at 0° and 100° C.
Air	1	1·36706
	3·447	1·36964
Hydrogen	1	1·36613
	3·349	1·36616
Carbonic Acid	1	1·37099
	3·316	1·38455

We will return to this subject when we come to consider Thermodynamic principles as applied to the different states of matter.

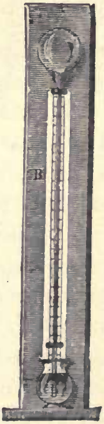
130. *Résumé* of §§ 117—129. Dilatation of Liquids; especially Mercury and Water. Carbonic Acid. Dilatation of Gases. Laws of Boyle and Charles. Another hint of an Absolute Zero of Temperature. Regnault's results as to change of volume under constant pressure, and change of pressure at constant volume—for different gases.

CHAPTER VII.

THERMOMETERS.

131. It seems now certain that the first inventor of the thermometer was Galileo, before 1597 (see *Mémoire sur la Détermination de l'Échelle du Thermomètre de l'Académie del Cimento*, par G. Libri, *Ann. de Chimie*, xlv. 1830). His thermometer was an air-thermometer, consisting of a bulb with a tube dipping into a vessel of liquid. The first use to which it was applied was to ascertain the temperature of the human body. The patient took the bulb in his mouth, and the air, expanding, forced the liquid down the tube, the liquid descending as the temperature of the bulb rose. From the height at which the liquid finally stood in the tube, the physician could judge whether or not the disease was of the nature of a fever.

A similar instrument was afterwards used, for a similar purpose, by the physician Sagredo, who, till recently, was regarded as the inventor of the thermometer.



Air-thermometers, however, are affected by changes in the pressure of the atmosphere, as well as by changes in the temperature of the enclosed air, and therefore, unless this disturbing cause is removed or accounted for, the reading of the thermometer is of no value.

Thermometers, containing a liquid hermetically sealed up in glass, were first made under the direction of Rinieri (died 1647), by Giuseppe Moriani, who, for his skill in glass-blowing, was surnamed Il Gonfia.

Many of the readings recorded by Rinieri are to be found in the *Memoirs of the Academy del Cimento*, but these were long supposed to have lost their value, as the instruments themselves could not be compared with our present thermometric scale.

In 1829, however, a number of these very thermometers were found by Antinori, and their graduations were compared with those of Réaumur's scale, so that the readings of Rinieri can now be interpreted.

One of the physical researches for which the Florentine Academy employed these thermometers, was to determine whether the melting of ice always takes place at the same temperature. This question they finally answered affirmatively.

The next great step in thermometry was made by Newton, in his *Scala graduum Caloris*, in the *Philosophical Transactions* for 1701, where he proposes the melting of ice and the boiling of water as standard temperatures.

132. Fahrenheit of Dantzic, about 1714, first constructed thermometers of which the graduation was uniform. These thermometers were much used in England, and Fahrenheit's graduation is still the most common in English-speaking countries. In Fahrenheit's scale the temperature of melting ice is marked 32°, and that of boiling water 212°.

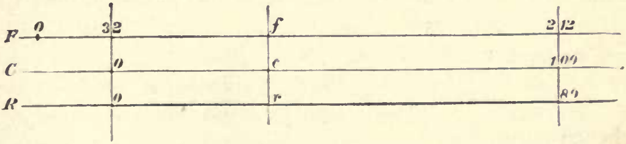
The Centigrade scale was introduced by Celsius, of Upsala. In it the freezing-point is marked 0°, and the boiling point 100°. The obvious simplicity of this mode of dividing the space between the points of reference has caused it to be very generally adopted, along with the French decimal system of measurement, by scientific men, especially on the Continent of Europe.

The scale of Réaumur, in which the freezing-point is marked 0°, and the boiling point 80°, is still used for some medical and domestic purposes on the Continent of Europe.

The existence of these three different thermometric scales furnishes an example of the inconvenience of the want of uniformity in systems of measurement.

The division of the range from freezing to boiling points into 180°, was probably in imitation of the division of a semicircle into 180 degrees of arc. This arose from the fact that 360 has a great number of divisors.

The selection of Fahrenheit's zero probably arose from its being supposed that the ordinary freezing mixture of ice and salt gives the lowest attainable temperature. If we suppose the same thermometer to have these three separate scales adjusted to it, or (still better) engraved side by side upon the tube, we easily see how to reduce from one scale to the other.



For, if f, c, r be the various readings of one temperature, it is obvious that

$f - 32$ bears the same ratio to (212—32 or) 180,
that c bears to 100,
and r bears to 80.

Hence

$$\frac{f - 32}{180} = \frac{c}{100} = \frac{r}{80}$$

[So far, all is legitimate and also necessary. But, in this latter half of the 19th century, the progress of science (!) seems to demand that, in Britain at least (for quasi-Chinese examination purposes), "problems" should be set, wherever a tempting opportunity like this presents itself.

To prepare the student for such an ordeal, we append a couple of possible specimens, with their solutions. These specimens are not of more than average grotesqueness, and scarcely of average absurdity; but we cannot devote more space to such things, *useful* as they may be.

Thus, to find the temperature which has the same numerical expression in the Fahrenheit and Centigrade scales, put f for c or c for f, and we have

$$\frac{f - 32}{180} = \frac{f}{100},$$

so that

$$f = c = - 40^\circ.$$

Again, to find the temperature whose Centigrade reading is the sum of its Fahrenheit and Réaumur readings, take

$$c = f + r,$$

and we have

$$c = 32 + \frac{180}{100} c + \frac{80}{100} c,$$

whence

$$c = - 20. \quad \text{Also, } f = - 4, \; r = - 16.$$

We do not exaggerate, when we say that practice at rubbish like this may turn the scale in some competitions for desirable appointments.]

133. The glass tubes for liquid thermometers are drawn, not bored, and it is therefore necessary to go through the

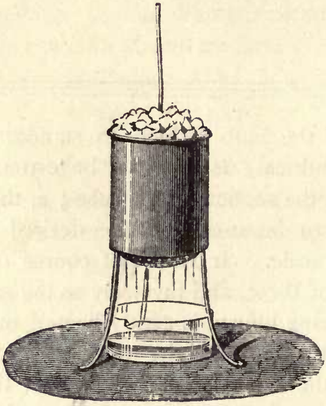
process of *calibrating* them:—first, roughly, in order to reject all that are not nearly uniform in bore throughout; then more carefully, so as to discover and tabulate the defects of the selected tube.

This is a very simple process. It consists in introducing a little column of mercury an inch or two in length; and, by slightly inclining the tube, causing it to slide from point to point, and measuring its length in each successive position. The narrower the bore at the place occupied by the mercury, the longer will be the column. These records are taken into account in graduating the tube by the help of a dividing engine.

The size of the bulb (which, in standard instruments, is usually cylindrical) is then to be estimated by three quantities:—1, the section of the tube; 2, the expansibility of the liquid to be used; 3, the desired length of one degree of the scale. It varies of course directly as the first and third of these, and inversely as the second.

The bulb, being blown, is gently heated in a spirit-lamp to expel a little air, and the open end of the tube is plunged into the liquid to be used. As the bulb cools, some of the liquid is forced into the stem by atmospheric pressure: and, on erecting the instrument, part of it passes into the bulb. This portion of liquid is now made to boil freely so that its vapour expels the air, and the end of the tube is again suddenly immersed in the liquid. When the whole has cooled both bulb and stem are filled with the liquid, and the excess is expelled by again warming the bulb. The liquid is once more boiled so as to expel the air from the stem, and the end of the tube is then hermetically sealed. Thus, in a properly filled thermometer, when it lies horizontally, the contained liquid is subject to the pressure of its own vapour only.

134. It is always desirable to have the range of a mercurial thermometer made long enough to include both 0° and 100° C. When this cannot be done, or when instead of mercury there is a liquid which boils at a lower temperature than water, definite points of the scale must be determined by careful comparison with a standard instrument.



When the range is long enough, the cardinal points of the scale are determined as follows :—

Freezing-point. The bulb and part of the stem of the instrument are immersed, as in the sketch, in pounded ice, from which water is dripping away, and left for some time, till the upper surface of the mercury, which is just visible above the ice, is observed to take a definite position. This is carefully marked *on the glass tube* as the zero-point; or, if the graduation has been previously effected according to an arbitrary scale (taking account of the calibration § 133), the zero-point is carefully observed and registered.

Boiling point. The instrument is now to be immersed, as carefully as possible, in steam freely escaping from water boiling under a pressure of 1 atmosphere. It is found that the temperature of boiling *water* is not steady, but that the temperature of the escaping steam is so. The annexed cut shows fully the arrangement usually adopted, and requires no explanation; but we must show how to define accurately what is meant by a pressure of 1 atmosphere. (See § 61, footnote.)

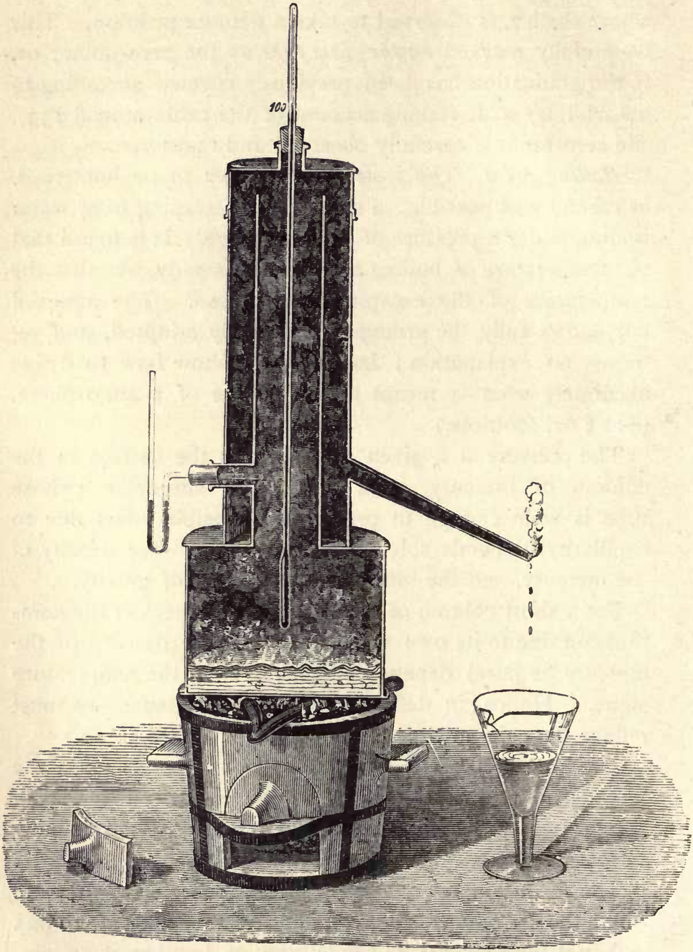
The pressure at a given depth under the surface in the column of mercury of a well-filled barometer (whose tube is wide enough to prevent any sensible effect due to capillarity) depends solely upon two things—the density of the mercury, and the intensity of the force of gravity.

For a short column of mercury we may neglect the compression due to its own weight, so that the density (if the mercury be pure) depends practically upon the temperature alone. Hence, in defining barometric pressure, we must reduce the column to its length at 0° C. (See § 120.)

The intensity of the force of gravity depends upon the latitude, and upon the height above the mean sea-level. Hence, both of these must be taken into account in defining an "atmosphere."

The definition, agreed on in this country, is the pressure when the barometer, reduced to 0° C., stands at 29·905 inches at the sea-level, in the latitude of London.

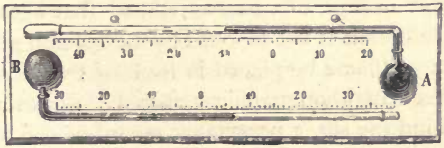
The change of pressure, per degree of temperature of the


100

boiling-point of water, in the neighbourhood of 100° C., is about 1·071 inch. It is rather less for temperatures lower than 100° C., and rather more for temperatures above that point. But the single number just given suffices for the practical determination of boiling-points near the sea-level. The further discussion of this question must be deferred till we are dealing with *Changes of Molecular State* due to heat. (See below, § 165.)

135. The mercurial thermometer is useful through a range of temperature from a little above the melting point (—40° C.) of mercury, to a few degrees below its boiling point (350° C.). When we desire to estimate temperatures about or below —40° C., alcohol is the liquid generally employed, as its freezing-point is about —130°C. For temperatures much over 300° C. recourse must be had to an air-thermometer; or, for rough purposes, to Pyrometers (§ 108), or Thermo-electric processes. When a thermometer of great sensitiveness is required for use at ordinary temperatures, carbonic acid is obviously (§ 122) a suitable liquid.

The contrivances for what are called *maximum* or *minimum* thermometers—*i.e.* instruments to record the highest or lowest temperature during a given time—are practically innumerable. The simplest, and most common, depend upon capillary forces. A column of mercury, pushing before it a little iron index (which it does not wet), is usually employed in a maximum thermometer;—a column of alcohol



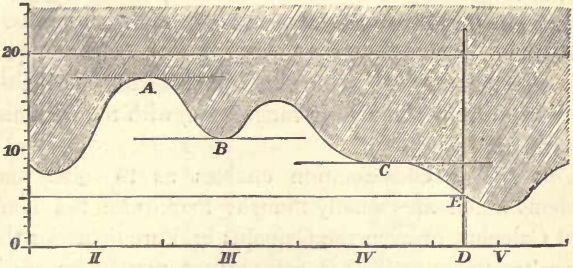
pulling back with it a little index of enamel (which it thoroughly wets), is usually employed for a minimum instrument. The force in either case is due to the tendency of the surface-film of the liquid to preserve the smallest area possible under the conditions to which it is subject. Other principles are employed, such as for instance a maximum thermometer in which the mercury has to pass through a very narrow part of the tube near the bulb. While expanding, it passes freely: but as soon as it begins to contract the column breaks at the narrow neck, and remains in the tube as a record of the highest temperature reached.

136. But all these devices are excessively imperfect, at least in comparison with *continuous* registration. This must, of course, be automatic. Many ingenious devices have been introduced for the purpose, but they are entirely superseded by the introduction of photography. The photographic process is so simple, and valuable, and at the same time so instructive, that we will devote a section or two to an explanation of it, and of some of its elementary consequences.

It is applicable of course, not to temperature alone, but to every variable quantity which can be suitably indicated by an instrument—such as (for instance) the barometer, the electrometer, or the variation compass.

Suppose the stem of a mercurial thermometer to be placed close in front of a narrow slit, so that light can pass only where the slit is not blocked by the column of mercury. Then, if a gas flame be placed in front of the thermometer, and a sheet of photographic paper be drawn uniformly along behind the slit, a permanent record of the successive positions occupied by the mercury will be formed by the boundary between the blackened and the unaltered parts of the paper. The clockwork by which the paper is drawn along is easily made to mark it at every hour or minute, and the graduations of the thermometer, or some known marks made on its stem, may easily be recorded photographically.

When such a sheet has been taken off, developed, and fixed, it presents an appearance somewhat like the sketch below:—



To find then what was the temperature at any instant, say $4^h.41^m$, all we have to do is to draw (as in the figure) the line *DE* which at that time must have coincided with the slit. The point *E*, where this line meets the boundary of the blackened part of the paper, indicates where the end of the mercury column was at the given instant. In the figure, as drawn, the temperature is $5^{\circ}\cdot 2$.

137. If we look at the diagram above, we see that the portion of the curve drawn obviously contains two *maxima* and three *minima*; and we see that the characteristic of either kind of point is simply that the tangent to the curve shall at that point be horizontal, *and shall not pass through the curve.* At a maximum, such as *A*, the tangent is horizontal, and (near *A*) wholly in the blackened space *above* the curve. Near a minimum, as *B*, it is wholly in the white space *below* the curve.

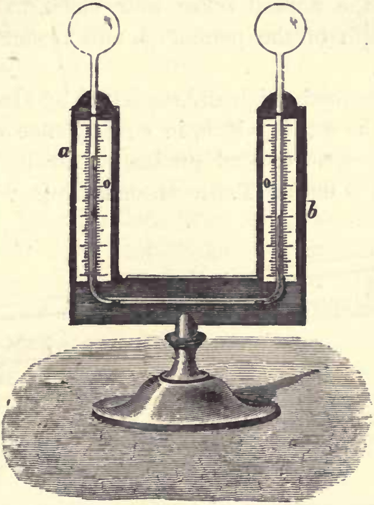
But a point such as C in the sketch is obviously neither a maximum nor a minimum, although the tangent is horizontal. At one side of C it is above, at the other below, the curve.

Another way in which this may be put, and which is in fact quite obvious from the behaviour of the thermometer itself, is the statement that *between two equal values of any varying quantity there always necessarily lies a maximum or a minimum.* Therefore the nearer together (in point of time) are these equal values, the more nearly does either coincide (in time, and also in magnitude) with the maximum or minimum sought.

[This simple consideration enables us to solve many problems which are usually thought to require the Differential Calculus, or even the Calculus of Variations, for their proper treatment. Thus it suffices not merely for the investigation of the law of refraction from the assumption that light takes the least time possible to pass from one point to another, but also for the investigation of brachistochrones, or lines of swiftest descent.]

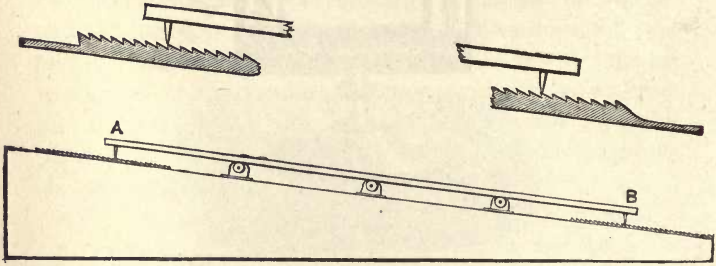
138. The general principle on which air-thermometers are constructed, is easily apprehended from the sketch of Balfour Stewart's apparatus in § 127. If a metal ball be employed, as in fact must be done if very high temperatures are to be measured, the gas must be preserved at *atmospheric pressure*, else there is danger of diffusion through the metal. Even in the case of a glass ball the constant pressure is desirable, not however on account of the permeability of the glass, but because of the alteration of its volume by increased pressure from within. There is not, as yet, any one particular form of air-thermometer which is in general use; all the greater experimenters having devised special forms for the special inquiries they had on hand.

The *Differential Thermometer* of Leslie and Rumford is really a couple of air-thermometers working against one another. In its simplest form it consists merely of a tube with a ball blown at each end. These balls contain air, and the contents of the two are kept separate by a column of sulphuric acid, whose motions indicate differences of pressure, and therefore of temperature, in the two bulbs. This instrument is obviously unaffected by changes of barometric pressure; it can be made very sensitive, and it is therefore of great use. Leslie made all his experiments on radiation of heat with this instrument; and, by varying the materials of which the balls (or one of them) were made, he converted it into a hygrometer, a photometer, an æthrioscope, &c.



139. The *Mean* or *Average* temperature during any assigned period can be obtained very accurately from the photographic record above described. Another method is to use a clock whose pendulum is not compensated (§ 105); and, from the gain or loss of time which it shows as compared with the normal mean time clock, to calculate the average length of the pendulum, and thence the average temperature.

Another method, originally suggested by Moseley's observations on the way in which, in consequence of alterations of temperature, sheet lead gradually tears itself off from a sloping roof, is that of T. Stevenson's *Creeper*. It is simply a flat bar of an expansible metal, provided with equidistant rows of teeth along its upper and lower ends, and made to rest on an inclined slab of slightly expansible material, in which horizontal grooves are cut as close to one another as possible.



The teeth and grooves are so shaped as to offer very slight resistance to motion upwards, while preventing all sliding down. When the instrument is raised in temperature it expands; and, as the lower end cannot move downwards, the upper end must rise, so that its teeth reach a higher groove. On the other hand, when it contracts by cooling, the lower teeth must be drawn up into a higher groove, because the upper end cannot slide down. It is obvious from this description that the "creeper" gives a record depending mainly upon the number and extent of the *fluctuations* of temperature. How it acquires the potential energy, which it has in its elevated position, is a question to be treated later.

140. *Résumé* of §§ 131—139. Invention of the Thermometer. Newton's Fixed points. Scales of Fahrenheit, Celsius, and Réaumur. Calibration, Graduation, and Filling of Liquid Thermometers. Determination of Fixed points. Air Thermometer. Definition of "an Atmosphere." Ranges of different Thermometers. Maximum and Minimum Thermometers. Photographic Registering Thermometers. Properties of a Maximum, of a Minimum, and of a Maximum-Minimum. Differential Thermometer. Averaging Thermometers. The Creeper.

CHAPTER VIII.

CHANGE OF MOLECULAR STATE. MELTING AND SOLIDIFICATION.

141. In sections 45 and 48 above we have given a general sketch of the part of the subject to which this chapter is devoted. The student is recommended to re-read these sections before proceeding further. When a similar recommendation has to be made, it will be put simply in the form "Refer again to §§—, —."

142. *Melting.* In accordance with the principle of § 9, and the fundamental principle of § 1, it is found that pressure and temperature alone require to be taken into account in the discussion of the melting of any definite solid. Hence the experimental law :—

The pressure remaining the same, there is a definite melting-point for every solid; and (provided the mass be stirred) however much heat be slowly applied, the temperature of the whole remains at the melting-point till the last particle is melted.

This is one of the bases of Black's doctrine of *Latent Heat.* Our modern knowledge that heat is not matter leads us to regard the energy which escapes detection by the thermometer as being employed in tearing asunder the particles of the solid. This will not appear very startling if we think of the work required to reduce a mass to fine powder, every particle of which is still a portion of the solid. But the first clause of the statement leads to the important question of the influence of pressure upon the melting-point. This was first discovered by James Thomson, in 1849, and his calculations with regard to the lowering of the melting-point of ice by pressure were exactly verified experimentally by Sir W. Thomson in the same year. Hopkins, Bunsen, and others, have experimentally determined the elevation by pressure of the melting-points of substances which *expand* on becoming liquid.

143. As an instance showing the nature of the experimental bases on which this statement rests, we refer again to the process of determining the zero-point of the thermometer (§ 134). There nothing is said about the *rate* at which the ice is melting:—*i.e.* about the quantity of heat supplied in a given time. See also § 131.

Water and mercury can be procured in very great purity, but the same statement cannot be made about the majority of other substances. Hence we give (as in § 104) only a short table of examples of approximate

MELTING-POINTS.

	Temperature C.
Ice	0°
Mercury	—40
Sulphur	111
Lead	335
Wrought Iron	1500 (?)

Some metallic alloys, especially those containing bismuth (which have received the general name of "fusible metal"), melt at temperatures considerably under 100° C. The recently discovered metal, *gallium*, melts at about 30° C. On the other hand, platinum cannot be fused in any ordinary furnace; and gas-coke (a form of carbon) has been softened only, not melted, by the most intense heat yet produced artificially—that of the electric arc.

144. As already stated, the effect of pressure upon the melting-point of a body was deduced from theory, and subsequently verified by experiment. The reason of its having previously escaped experimenters is probably to be found in the extremely small amount of the effect even when great pressures are applied. This is not the place to enter upon the theory, which will be discussed later; but we may mention the theoretical result in the form that

Bodies which contract in the act of melting have their melting-points lowered by increase of pressure, and vice versâ.

145. The theoretical result for ice, exactly verified by experiment, is a lowering of the melting-point by

$$0^\circ\!\cdot\!0075 \text{ C.}$$

for each additional atmosphere (§ 134) of pressure. This may be roughly stated in the form that, under a pressure of *one ton weight per square inch*, ice melts at *one degree Centigrade* under its ordinary melting-point.

[Along with this we have to remark that the density of ice is only about 0·92 of that of water, so that water-substance contracts by eight per cent. in the act of melting.]

Many of the consequences of this important fact were familiar to all before the fact itself was pointed out.

One form in which it must have been well known for hundreds of years is the form in which we try the same experiment every time we make a snowball. Schoolboys know well that after a very frosty night the snow will not "make":—their hands cannot apply sufficient pressure. But, if the snow be held long enough in the hands to be warmed nearly to its melting-point, it recovers the power of "making," or rather of "being made." Every time we see a wheel-track in snow we see the snow is crushed, and even after one loaded cart has passed over it,—certainly after two or three have passed,—the snow has been crushed into clear transparent ice. The same thing takes place by degrees after people enough have walked over a snow-covered pavement; and in all these cases this minute lowering of the freezing-point has led to the result. And now we see how it is that the enormous mass of a glacier moves slowly on like a viscous body, because in consequence of this most extraordinary property it behaves under great pressure precisely as if it were a viscous body. The pressure down the mass of a glacier must of course be very great, and as the mass is — especially in summer — freely percolated throughout by water, its temperature can never (except on special occasions, and then near the free surface) fall notably below the freezing-point. Now, in the motion of the mass on its journey, there will be every instant places at which the pressure is greatest,—where in fact a viscous body, if it were placed in the position of the glacier ice, would give way. The ice, however, has no such power of yielding; but it has what produces quite a similar result—wherever there is concentration of pressure at one particular place it melts, and as water occupies less bulk than the ice from which it is formed, there is immediate relief, and the pressure is handed on to some other place or part of the mass. The water is thus relieved from the pressure by the yielding caused by its own diminution of bulk on melting. The pressure is handed on; but the water remains still colder than the freezing-point, and therefore instantly becomes ice again. The only effect is that the glacier is melted for an instant at the place where there is the greatest pressure, and gives way there precisely as a viscous body would have done. But the instant it has given way and shifted off the pressure from itself it becomes ice again, and that process goes on continually throughout the whole mass; and thus it behaves, though for special reasons of its own, *precisely* as a viscous fluid would do under the same external circumstances.

The first who seems to have realised this on a small scale by experiment was Dollfuss-Ausset, who showed that by compressing a number of fragments of ice in a Bramah press, it was possible to melt them; and when pressure was taken off them, to allow them to revert again into a solid block. But he found that with very cold ice the experiment did not succeed. In fact, as we now see, even with his Bramah press, he could not apply pressure enough.

By opening a hole in the end of a cylinder in which snow is compressed by a Bramah press, we obtain a cylinder or wire of solid ice gradually squeezed through the hole, just as wires are made of soft or crystalline metals. The mechanism of the process is different, but the results are exactly the same.

Another simple but effective experiment may be made by passing a loop of wire round a bar of ice supported horizontally. A weight attached to the wire pulls it gradually through the ice, which melts before the wire and is immediately re-formed behind it: so that the wire passes entirely through (as in cutting cheese or soap) and yet leaves the bar as strong as ever.

146. Every one knows that when melted bees-wax partially solidifies, the crust if broken sinks in the liquid. The same phenomenon is observed in lava-lakes such as that of Hawaii, where the crust " cracks in different directions, and first one half of the lake and then the other is covered with

a fresh coating of red-hot lava, the crust tumbling out of sight as it shrunk and cracked in cooling." *

Just as the effect of pressure on the melting-point of ice enables us to account for the plasticity of glacier ice, so the effects now described enable us to explain with great probability why it is that the materials forming the interior of the earth are practically rigid, and therefore solid, though at temperatures far above their ordinary melting-points.

For, as will be seen when we consider (under the head of *Conduction*) underground temperatures, there can be little doubt that the temperature at a few hundred miles below the earth's surface must be very high—certainly far above the usual melting-point of lava. Yet, as Sir W. Thomson has shown from the amount of the tides, there can be no doubt that, as a whole, the earth is nearly as rigid as a globe of steel of the same size.

These two apparently inconsistent conditions are at once reconciled, if we suppose the average materials of the earth to be such as, like lava, to expand on melting:—for the immense pressure to which they are subjected from superincumbent strata is probably sufficient to raise their melting-point above their present temperature. Thus they may remain solid, even at a white-heat. But if by the cooling and shrinking of the lower strata within the solid crust this pressure should be anywhere considerably relieved, the mass affected would (almost explosively) melt with considerable expansion. This seems to have important bearings on earthquakes and upheavals.

[It may be mentioned, in passing, that if the earth were liquid throughout, and of *uniform* density equal to its present mean density, the pressure within a few hundred miles

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* J. W. Nichol, *Proc. R. S. E.*, 1875–6, p. 117.

of the surface would increase at the rate of somewhere about 800 atmospheres (or nearly $5\frac{1}{2}$ tons weight per square inch) per mile of depth.]

Hopkins has found that the melting-point of wax is raised about 10° C. by 500 atmospheres' pressure; and Bunsen gives a rise of $3^{\circ}\cdot5$ C. as the effect of 100 atmospheres on the melting-point of paraffin.

147. We must now consider the second clause of the experimental statement of § 142.

That the temperature of the mixture of solid and liquid should remain at the melting-point, however much heat be supplied, till the last particle is melted, was explained by Black (on the hypothesis of the materiality of heat) by the supposition that the liquid differs from the solid simply by having taken into combination a certain proportion of caloric. Thus the liquid was regarded as a species of chemical combination of the solid with an equivalent of caloric. As no effect was produced on the temperature of the body by this admixture, Black introduced for this supposed equivalent of caloric the name of *Latent* Heat. Relatively to the knowledge of his time, the name was a felicitous one, because it was found that when a liquid solidified it gave out exactly as much heat as it had taken in on melting.

Unfortunately, from our modern point of view, the term is not a felicitous one—and yet it is so ingrained in our language (like *vacuum* and *centrifugal force*) that we are not at all likely soon to get rid of it. But no difficulty will be found if we keep in mind that when we speak of latent heat we mean no more than this—that a certain amount of heat is in every case required to change the molecular state of a substance even when there is no alteration of its temperature.

148. We are, as yet, almost wholly ignorant of the form in which energy exists in bodies generally; and a great deal of mischief has been done (almost ever since the time of Black) by the assumption that bodies must possess a certain amount of what has been called "sensible," or "thermometric" heat. Until we know, at least partially, the nature of the internal mechanism connecting the particles of matter, it is altogether vain to discuss questions concerning the heat present in a body, farther than is involved in estimating the amounts of energy supplied to it, and given out by it, in the various stages of an operation. Refer again to § 74.

149. But if we consider for a moment the amount of work necessary to grind to fine powder even the most friable of solids, and, going farther, think what almost infinitely more perfect breaking up befalls such solids when they are melted, it is easy to see how a great part of the energy, supplied to a solid in the form of heat, must be applied to the mere mechanical work of pulling its particles into the position of comparatively slight constraint which they occupy in the liquid, against the molecular forces which originally maintained them in the solid form.

150. With these explanations, we retain the term *Latent Heat* as a general one—applicable in all cases of change of molecular state—where energy *in the heat form* can be supplied to a body without producing alteration of its temperature.

[The student should carefully notice the words in italics, for the same amount of energy can be given to the ice in many other ways, without either melting it or changing its temperature—*e.g.* by lifting it to the proper height against gravity, or by projecting it with the proper velocity.]

Thus the *latent heat of water* is to be numerically measured as *the number of units of heat* (§§ 55, 56) *which must* *be communicated to a pound of ice at 0° C. to convert it into a pound of water at 0° C.*

This is (§ 9) evidently a definite quantity. For the temperature mentioned in the definition requires that the pressure shall be 1 atmosphere.

151. The experimental determination of this quantity can be made in many ways: but all the usual ones depend upon the direct comparison of the effects of equal amounts of heat upon ice and upon water.

The ordinary lecture-room form of the experiment consists in pouring over a pound of ice at 0° C. a pound of water at about 80° C., and carefully stirring the mixture. When proper precautions against loss of every kind are taken, it is found that under these circumstances the whole of the ice is just melted—the resulting temperature being still 0° C.

Assuming, what is very nearly the case, that the amount of heat required to raise the temperature of a pound of water one degree is the same throughout the whole range from 0° to 80° C., it is obvious that the pound of hot water has lost 80 units of heat, which must have gone to the pound of ice with the result of melting it without raising its temperature. Hence it follows that (in accordance with the definition of latent heat, § 150), 80 is the latent heat of water. It appears from the experiments of Person and others that the correct value is more nearly 79·25. The experimental part of the work presents no very great difficulty, but the mode of reasoning from the results depends to some extent upon the opinion we may form as to *whether the transition from ice to water is an abrupt or a gradual process.*

152. There can be no doubt that, in many substances at least, the transition from solid to liquid is gradual and not abrupt. Every one is familiar with the softening of wax and

paraffin, as they are gradually raised in temperature. The *welding* of iron and of platinum, at high temperatures, is another case in point. And several excellent authorities state their conviction that something analogous occurs with ice. What farther we have to say on this question will be profitably deferred till we discuss the whole subject on thermodynamic principles. It is clear that a rapid increase of specific heat, just below the melting-point, might, if undetected, lead to an over-estimate of the latent heat as we have defined it. But it is also clear that this explanation can only be valid if ice, from which water is trickling, is (all but its superficial layer) essentially a little colder than 0° C. Forbes and Balfour Stewart state that the temperature of a mass of ice, which has been rapidly pounded, is invariably found to be a little below the freezing-point.

153. Water is almost exceptionally high among liquids as regards the amount of its latent heat. The following short table gives some general notions on the subject :—

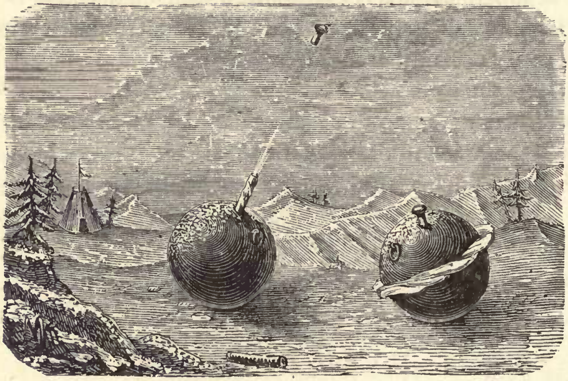
LATENT HEAT OF FUSION.

Water	79·25
Phosphate of Soda (crystallised)	67·0
Zinc	28·1
Sulphur	9·4
Lead	5·4
Mercury	2·8

It is to be observed that the numbers here given denote the units of heat required just to melt one pound of each of these substances without change of temperature.

154. We have already alluded to the abrupt changes of volume which usually take place on melting. In general, the change is of the nature of expansion; but water, cast-iron, type-metal, and some other bodies, contract. As the

process of solidification is exactly the converse of that of melting, it is accompanied by disengagement of latent heat and return to the former volume. Hence the nicety with which iron and type-metal adjust themselves to every little crevice in a mould. Hence also the bursting of water-pipes during (not, as the majority even of "educated" people still think, *after*) a frost. The pressure requisite to prevent water from freezing in a closed vessel, nearly full, is enormous, provided the temperature be a few degrees under the usual freezing-point: sufficient, as has been found by trial, to burst the strongest bomb-shells. The amount of work which can be done by a pound of water, in freezing under given circumstances, can be at least approximately calculated, as we will show when treating of the dynamical theory. In fact, while discussing the lowering of the freezing-point by pressure, we have pointed out (§ 145) that a pressure of a ton weight per square inch is requisite to prevent ice from being formed at a temperature even one degree under zero.



155. The process of solution of a solid in a liquid is, in so far at least as it is independent of chemical action, very closely analogous to melting; and, as in § 149, must obviously require a supply of energy. This is usually taken from the body itself and from the menstruum, as well as from surrounding bodies, in the form of heat.

Thus solution of a solid in a liquid is usually accompanied by cooling. This is, in some cases, partially or wholly masked, sometimes even overcome, by the heat developed by chemical action.

One of the commonest of these arrangements for producing cold (*i.e.* rendering heat latent), is to dissolve nitrate of ammonia in an equal weight of water. If both be taken at ordinary temperatures (say 10° C., or 50° F.), the temperature of the solution falls to about —15° C. A somewhat greater cooling is produced by pouring commercial hydrochloric acid upon snow.

But by far the lowest temperatures yet attained by such means are procured by pouring ether upon solid carbonic acid and other bodies which are gaseous at ordinary temperatures and pressures. These temperatures are further considerably lowered by placing the mixture under a receiver, and exhausting the air. Natterer estimates the lowest temperature he has thus obtained at about —140° C., more than half-way from freezing-point to absolute zero (§§ 96, 125). Perhaps even more striking results may yet be obtained from solid hydrogen.

156. When two solids, on being mixed as crystals or powder, melt one another, we have of course to supply from without the latent heat for each, except in so far as heat is chemically developed by the combination. Thus we explain the action of the well-known freezing mixture of snow and common salt, or of salt and pounded ice (§ 132).

If the salt has been previously cooled to 0° C., the temperature of the mixture falls to about —20° C.

157. Conversely, when a substance in solution crystallises out, we have in general a development of heat. This is very well shown by supersaturated solutions of sulphate or acetate of soda, which suddenly crystallise when the smallest fragment of the solid is dropped in. In the acetate of soda the water is almost entirely taken up by the solid as water of crystallisation.

158. *Résumé* of §§ 141–157.—Law of Melting. Effect of Pressure. Melting-points of some Solids. Behaviour of Ice and Lava. Consequences as regards Glaciers and the Strata under the Earth's Crust. Latent Heat of Fusion. Latent Heat in different Liquids. Solution. Freezing Mixtures. Heat developed in Solidification.

CHAPTER IX.

CHANGE OF MOLECULAR STATE. VAPORISATION AND CONDENSATION.

159. Refer again to §§ 46, 47. We have seen (§ 152) that it is not yet settled whether the change from the solid to the liquid state takes place *precisely* at the definite temperature called the melting-point or not. There is no doubt, however, that the transition from the liquid (and, in some cases at least, from the solid) state to the state of vapour takes place at all temperatures, but more freely the higher the temperature, up to the so-called boiling-point.

Every one must have noticed that even in the coldest winter day—especially if it be windy—the ice on the pavements gradually dwindles away, though constantly appearing solid and hard. It is, in fact, always evaporating though very slowly. Whether it passes or not through the liquid state in a thin film on the surface is not yet known. And distillation of liquids is often practised on a large scale, in manufacturing operations, at temperatures kept purposely below their boiling-points. Salt-pans form an excellent example. All but a very small fraction of the vapour constantly in the air, has been raised from the surface of oceans, lakes, or moist ground, at temperatures far below the boiling-point.

160. BOILING. Experiment enables us to state for this phenomenon a law precisely similar to that of § 142, viz.—

The pressure remaining the same, there is a definite boiling-point for the free surface of every liquid; and (provided the mass be stirred) however much heat be applied, the temperature of the whole remains at the boiling-point till the last particle is evaporated.

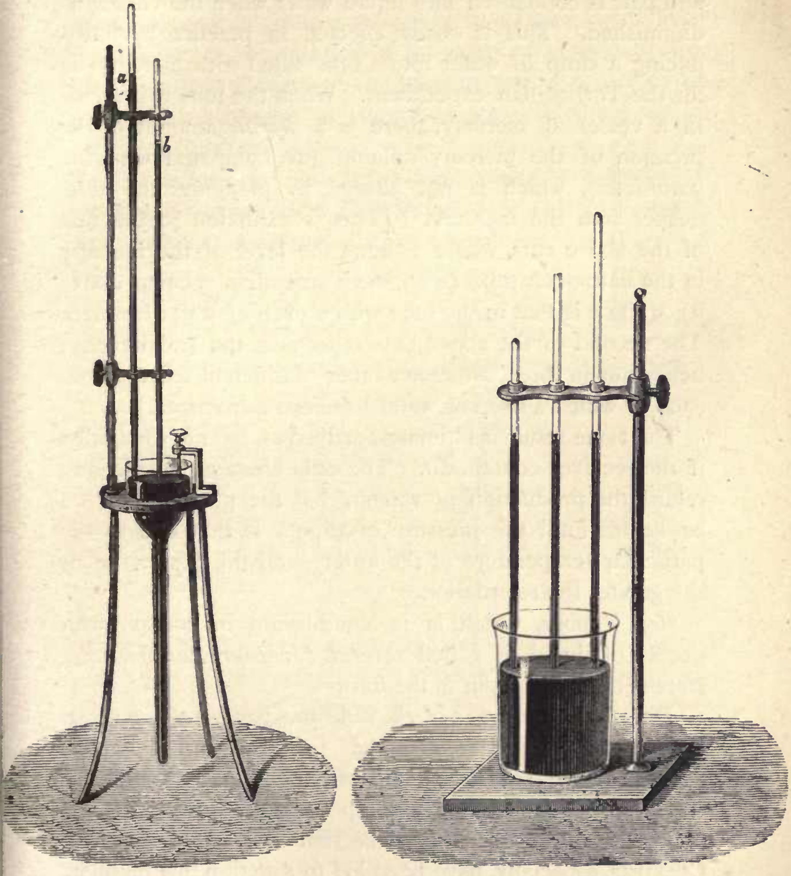
The effect of pressure upon the boiling-point can be calculated, as was that of pressure upon the melting-point; but as we do not know of a substance which (at the same temperature and pressure) occupies less bulk in the form of vapour than in that of liquid, we may assert that the effect of pressure is in all cases to *raise* the boiling-point.

So far as water is concerned, we have already (§ 60) given some explanations and experimental data on this subject. We will now treat the whole experimental law more fully, and in a manner similar to that which we adopted for the analogous law of melting.

161. We take water vapour as a type—as it is the most important, and has been therefore the most carefully studied. The first even approximately accurate statement of its behaviour is due to Dalton. Numerical data of great precision, and extending through a wide range of temperatures and pressures, have recently been furnished by Regnault. And an experimental result of startling novelty, and of the greatest theoretical importance, due to Andrews, revealed, so lately as 1869, what is the true distinction between a vapour and a gas.

162. If a vessel of water be placed in an exhausted receiver, evaporation will immediately commence, and the process will go on with great rapidity until the pressure of the vapour in the receiver rises to a certain definite amount, which is found to depend solely upon the temperature.

If the receiver is fitted with a piston, which is pushed in



or pulled out so as greatly to increase or to diminish its volume, still the pressure of the vapour remains unchanged;

for fresh vapour is formed when the volume is increased, and part is condensed into liquid water when the volume is diminished. This is easily effected in practice by introducing a drop of water into a tube filled with mercury, as for the Torricellian experiment. When the tube is inverted in a vessel of mercury, there is a *definite* amount of depression of the mercury column (as compared with the barometer), which is not altered by plunging the tube deeper into the mercury. [This is exhibited in the first of the above cuts, where *a* shows the level of the mercury in the barometer tube (with the Torricellian vacuum above it), while *b* is that in the tube with a drop of water inserted. The second of the above cuts represents the simultaneous behaviour in three barometer tubes of different lengths, into each of which a drop of water has been introduced.]

The same result is ultimately arrived at, but not so rapidly, if the receiver contain air. The only effect of the air is to retard the production of vapour, but the process goes on as before until the pressure of vapour is that due to the particular temperature of the water—and the denser the air the greater the retardation.

163. Vapour, which is in equilibrium in contact with excess of liquid, is called *saturated vapour*, and Dalton's statements may be put in the form—

The ultimate pressure of the saturated vapour of any liquid depends only upon the temperature.

[N.B.—The student should remark that in many old books, and in too many modern ones, the word *tension* is improperly used in this connection instead of *pressure.* Chemists, especially, have been led to sanction this blunder, and almost invariably speak of vapour-tension.]

164. While a liquid is thus in equilibrium with its own vapour, suppose the vapour to be removed by means of an

air-pump almost as fast as it is formed. Then, obviously, fresh vapour is furnished very rapidly from the liquid: and it is observed to come not merely from its surface, but in bubbles from the interior of the mass and specially from sharp points or edges of solids immersed in it. This free and rapid discharge of vapour is what is called *boiling*. And we thus see that—

The boiling-point of a liquid is the temperature at which its saturated vapour has a pressure equal to that to which the free surface of the liquid is subjected.

PRESSURE OF SATURATED WATER VAPOUR—REGNAULT.

Temperature C.	Pressure in Atmospheres.	Temperature C.	Pressure in Atmospheres.
0°	0·006	120°	1·962
10	0·012	130	2·671
20	0·023	140	3·576
30	0·042	150	4·712
40	0·072	160	6·120
50	0·121	170	7·844
60	0·196	180	9·929
70	0·306	190	12·425
80	0·466	200	15·380
90	0·691	210	18·848
100	1·000	220	22·882
110	1·415	230	27·535

165. On this very instructive table (given by Regnault at p. 728 of his magnificent *Rélation des Expériences*, etc., *Mém. de l'Ac. des Sciences*, 1847,) a few remarks may be made.

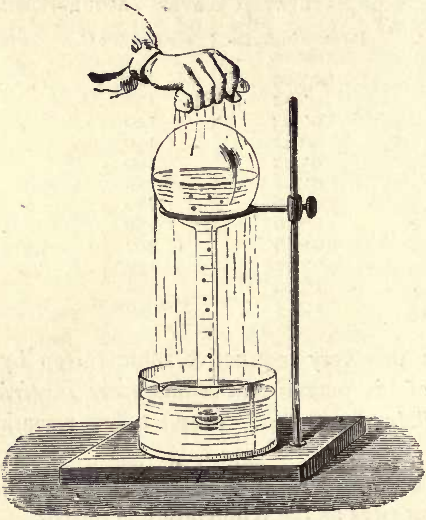
(*a.*) We see how very rapidly the pressure of saturated water-vapour rises as the temperature is raised.

Thus the rise of temperature from 100° to 180° increases the pressure from one to nearly ten atmospheres, while an additional rise of only 40° C. raises the pressure to nearly twenty-three atmospheres.

Compare this with the behaviour of a gas such as air

(§ 124), where the pressure (at constant volume) rises approximately in proportion to the absolute temperature; and we see how very much less dangerous, so far as the chances of an explosion are concerned, is an air-engine than a steam-engine working (with saturated steam) at the same high temperature.

(*b.*) Water at ordinary temperatures may be made to boil by placing it in the receiver of an air-pump and producing a sufficient vacuum. Thus if it be taken at 10° C. (50° F.) it will boil when the pressure is reduced to 0·012 of an



atmosphere (or, more accurately, to 9·16 millimetres of mercury). And a notable feature of this experiment is that the water is found to become gradually *colder* as the boiling proceeds, thus requiring farther exhaustion by the air-pump to maintain the process. This will be explained in a subsequent section, when we are dealing with the Latent Heat of steam.

A striking form of this experiment consists in making water boil in an open flask so furiously that the greater part of the air is expelled by the steam, then corking the flask and inverting it. When cold water is poured on the bottom of the inverted flask, it condenses the steam and thus diminishes the pressure on the water, so that it immediately begins to boil. Boiling water, poured on, at once stops the boiling. If the air has been very completely expelled, the boiling by the application of sufficiently cold water can be produced even when the contents of the flask have cooled to the temperature of the air of the room.

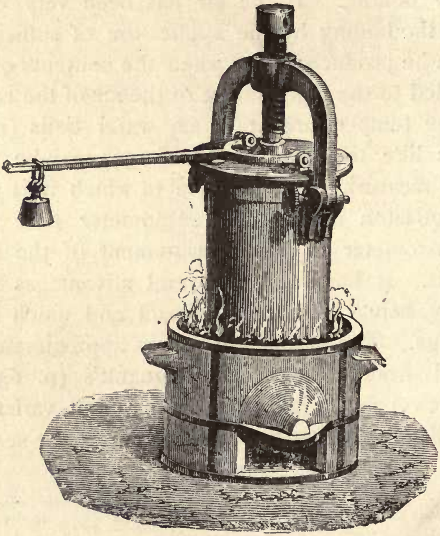
(*c.*) The temperature at which water boils (in a small apparatus like that sketched in § 134) may be used as a means of measuring the pressure to which it is subjected. Thus Wollaston made the thermometer take the place of the barometer in the measurement of the heights of mountains. It has, in fact, several advantages as regards portability, being far more compact and much less liable to breakage. The following roughly approximate formula, calculated from a table of Regnault's (p. 633 of the *Rélation*, etc.) shows how the boiling-point varies with the ordinary fluctuations of the barometer near the sea-level.

	Pressure.	
Temperature C.	Atmospheres.	Inches.
$99° \pm \tau$.	$0{\cdot}9647 \pm 0{\cdot}0348\,\tau$.	$28{\cdot}87 \pm 1{\cdot}04\,\tau$.

[This formula must not be employed for values of τ much exceeding 2. For greater ranges, or for more accurate values within this range, Regnault's full table must be consulted.]

Roughly speaking, the boiling-point of water is lowered by 1° C. for 960 feet of vertical ascent above the sea-level. At the top of Mont Blanc the *Hypsometric Thermometer* was found by Bravais and Martins, in 1844, to stand at 84°·4 C.

(*d.*) We see why a diminution of pressure reduces the solvent and cooking powers of boiling water, while an increase of pressure exalts them. Tea prepared at the top of Mont Blanc is poor stuff; and *Papin's digester*, which is used for extracting everything soluble from bones, etc., is simply a very strong boiler, in which water, under the pressure of its saturated vapour, can be safely raised to temperatures far above its ordinary boiling-point.



166. Approximate expressions for the amount of heat rendered latent in the evaporation of water at different temperatures were given by Watt and others. But the subject remained doubtful until Regnault cleared it up. He gives for what he calls the *total heat of steam*, at any temperature t° C. the very simple formula—

$$606{\cdot}5 + 0{\cdot}305\, t.$$

Thus a pound of saturated water vapour at 0° C. gives out 606·5 units of heat in condensing to water at 0°; while if its temperature had been originally 100° C. it would have given out 606·5 + 30·5 (or 637 units) in passing to water at 0°.

In the next chapter the (very small) variation of specific heat of water with temperature will be treated. When it was taken into account along with the above formula, it was found by Regnault that the latent heat of steam at different temperatures falls

from 606·5 at 0° C.,
to 536·5 at 100°,
and to 464·3 at 200°.

The latent heat at any temperature is here the number of units of heat required simply to convert a pound of water into steam of the same temperature.

For most practical purposes this may be taken as indicating a decrease simply in proportion to the rise of temperature, and amounting to 11·5 per cent. for each hundred degrees above the freezing-point. Watt's hypothetical statement was to the effect that the heat required to change a pound of water at 0° C. into steam at any pressure whatever —*i.e.*, the total heat of steam—is constant. If this were true the sums of the last three pairs of numbers should be approximately equal. They are not so, and they show that Watt's statement involves an error in defect amounting to about five per cent. of the whole for every hundred degrees above 0° C.

When we are dealing with the dynamical theory, we shall have occasion to discuss this question more fully.

167. According to Andrews, the latent heat of a pound of vapour, produced from certain common liquids by boiling at the ordinary atmospheric pressure, is as follows:—

LATENT HEAT OF EVAPORATION AT 1 ATMOSPHERE PRESSURE.

Water	536·0
Alcohol	202·4
Ether	90·5
Bromine	45·6

Here, again, water stands relatively very high. And, as we have already seen that the latent heat of steam increases as the temperature of evaporation is lower, we see what a very large amount of heat is required for the evaporation going on over the oceans; and how great is the amount of heat set free when that vapour is condensed into fogs or clouds. This leads us to consider the phenomenon of condensation with some of its consequences.

168. A striking illustration of the great latent heat of steam is given by a very simple arrangement. We have merely to lead steam from a boiler into a vessel containing a measured quantity of ice-cold water. At first, the steam is condensed as soon as it reaches the water; but as the water becomes warmer the steam gradually advances from the end of the conducting pipe, forming an increasing bubble at whose surface condensation is steadily going on. As soon as the water is raised to the boiling-point, the

steam passes freely through it. When this stage is reached, remove the steam-pipe and measure the volume of the water. It is found to have increased by less than a fifth of its original amount. This increase is, of course, in a condensed form, the steam, whose latent heat has raised by 100° C. the temperature of the mass of water.

169. The latent heat of vaporisation is utilised in many ways, especially for cooling and for freezing.

Thus water, put into a vessel of unglazed clay, is kept permanently cool in warm dry air, by the evaporation from the surface of the vessel. A similar result is produced when a glass vessel is employed, if it be wrapped in a wet cloth and placed in a current of air. In some parts of India ice is procured by exposing water at night in shallow unglazed saucers, laid upon rice-straw. More rapid effects may, of course, be obtained by using instead of water highly-evaporable liquids such as sulphuric ether. A few drops of ether, sprinkled on the bulb of a thermometer, produce an immediate contraction of the contents, which is greater as the temperature of the air is higher. The cooling of water, when it is made to boil at low temperatures (by reducing the pressure, as in § 165 (*b*)) is due to the same cause. This process, with a quantity of dry oatmeal or a large surface of sulphuric acid (to absorb the vapour as it is formed) was employed by Sir John Leslie for the purpose of making ice; and is still, with various modifications, the basis of some of the most convenient domestic ice machines.

The Cryophorus (whose principle will be explained when we are dealing with Daniell's Hygrometer, § 172) is another very curious illustration of the same fact.

When a jet of carbonic acid, liquefied by pressure, is allowed to escape into the air, the outer layers of the jet vaporise at once; taking the requisite latent heat from the core of the jet, which is thus frozen into a solid and can be collected in a proper receiver as a snow-like mass. It appears that hydrogen has in this way been obtained as a steel-grey powder. A very striking experiment of the same class is the freezing of water in a white-hot platinum dish. This is easily effected by the help of liquid sulphurous acid, which evaporates very freely from the water while it remains suspended above the dish in what is called the "spheroidal state" (§ 213). If the dish be not sufficiently heated the experiment fails.

Faraday succeeded in freezing even mercury in a white-hot vessel by a process of this kind. The mercury was in a little capsule resting on a mixture of solid carbonic acid and ether in the spheroidal state in a highly heated platinum crucible.

170. The reader will now easily understand why it is possible (as stated in § 155) to procure very low temperatures by exposing solidified carbonic acid, mixed with ether, in an exhausted receiver.

171. We must next consider the converse process, the condensation of vapour into liquid. And for the present, we confine our remarks to the behaviour of water-substance. In § 162 we have already shown that condensation commences, in a vessel containing water-vapour alone, as soon as the pressure of the vapour exceeds that corresponding to saturation. We may state this, of course, in another form, viz. that condensation commences as soon as the temperature falls below that corresponding, in Regnault's table, § 164, to the pressure of the water-vapour present. And it is found by experiment that the pressure of air or other gas does not modify this result except in more or less *retarding* it. Hence, if we present to air containing water-vapour a solid cooled below the temperature of saturation corres-

ponding to the vapour-pressure, condensation will take place in the layer of air immediately in contact with the solid, which will thus be covered with a film of *Dew*. This film will become thicker, until, by the latent heat given up by the vapour in condensing, the solid has been raised to the temperature of saturation corresponding to the vapour-pressure. If the solid be at a temperature below 0° C. the film freezes as it is deposited, and becomes what is called *Hoar Frost*.

In Hope's experiment (§ 121) the metal vessel containing the freezing mixture is rapidly covered with a layer of hoar frost, however warm the surrounding air may be, provided it contains a moderate amount of aqueous vapour.

172. The statements in last section show at once what is meant by the meteorological term, the *Dew-point*. It is the temperature at which saturated water-vapour would have the same pressure as that of the vapour present in the air at the time; and it could therefore be found directly from Regnault's table (§ 164) if we knew the quantity of vapour per cubic foot of air. But the converse process is that most commonly used, the dew-point being directly measured, and then employed for the purpose of estimating by Regnault's table the quantity of vapour present in the air at any time.

Daniell's *Hygrometer* is an ingenious instrument by which a body is gradually cooled, so that we can measure its temperature at the instant when dew just begins to be deposited on it. It consists of a glass tube with a bulb at each end. One of these bulbs is made of black glass, to show at once the slightest trace of dew on its surface. In this bulb is a thermometer (whose indications can be read through the clear glass tube joining the two bulbs) and a quantity of sulphuric ether The instrument-maker boils this ether; and hermetically seals the second bulb when the ether-vapour has expelled the air from the whole apparatus (as in § 165 (*b*)). To use the instrument, pour a few drops of ether on a piece of cambric wrapped round the second bulb. The evaporation of the ether cools this bulb and condenses the ether-vapour in it. More vapour is formed from the ether in the black bulb, and again condensed in the second bulb. Distillation in fact goes on between the two bulbs; and the black bulb, with its contents, becomes gradually colder on account of the latent heat required for the persistent formation of vapour. The temperature of the black bulb is read by the inclosed thermometer at the instant of the first appearance of dew. The thermometer is again read at the instant that the dew disappears, when the apparatus begins to be heated again to the temperature of the air. It is usual to assume the mean of these readings as the dew-point.

Suppose water to be put in the instrument instead of ether, and snow and salt instead of ether to be applied to the empty bulb. The rapid evaporation of part of the water from the full bulb freezes what is left. This is the Cryophorus (§ 169).

Another method of finding the dew-point is by the *Wet and Dry Bulb Thermometers.* Two similar thermometers are placed side by side; one having its bulb covered with cambric, connected by a few threads with a small vessel of water, so as to be kept constantly moist. The thermometer with the naked bulb shows the temperature of the air, the other shows a lower temperature, which differs from the first in consequence of the evaporation constantly going on from its moist covering. When the air is nearly saturated with moisture, the evaporation is very slow; and the lowering of temperature small. But if the air be dry, and especially if it be also warm, there is rapid evaporation and considerable lowering of temperature. Dr. Apjohn, who has studied this subject with particular care, gives for the determination of the dew-point by this arrangement the formula

$$p = p_0 - \frac{\delta}{48} \cdot \frac{b}{30}.$$

In this formula δ is the difference between the readings of the thermometers, p is the sought pressure of vapour in the air, p_0 that in Regnault's table corresponding to the temperature of the wet-bulb, and b is the height of the barometer in inches. To a certain extent this formula is, as yet, empirical. The full treatment of the question by theory remains to be discovered.

173. The theory of the formation of dew was first correctly given in Dr. Wells's *Essay* of 1814. It cannot be fully stated till we have dealt with *Radiation*. But it may suffice for the present to say that the cooling of stones, blades of grass, &c., by radiation, takes place most rapidly in clear, calm nights. Clouds, in general, radiate back a great deal of the heat they receive, and so prevent objects on the ground from cooling sufficiently. Winds also, unless the air is itself very cold, constantly warm again bodies cooled by radiation. Hence it is after clear, calm nights that the dew is usually most copious; and when the radiation has been sufficiently rapid we have it in the form of hoar-frost. The temperature of the air itself, near the ground, cannot at any time fall much below the dew-point; for, as soon as it does so, condensation takes place, and latent heat of vapour is set free.

174. What has been said in the preceding sections of the condensation of aqueous vapour is true, generally, of

the vapours of all substances which are liquid at ordinary temperatures and pressures. Some liquids, such as commercial sulphuric acid, have a scarcely measurable vapour-pressure under ordinary conditions; others, as sulphuric ether, evaporate with great rapidity.

But it is only within comparatively recent times that it has been shown experimentally that all gases are really vapours. This has been done by reducing them to the liquid, and sometimes even to the solid, state. Mere cold effects this with many substances, mere pressure with others; but some (especially those bodies which used to be called *permanent gases*) require the combined application of cold and pressure. Faraday effected the liquefaction of a great number of gases, mainly by pressure. On the other hand Cagniard de la Tour rendered liquids, with little change of density, gaseous (or, at all events, not liquid), by heating them under great pressure. It was Andrews, however, who first cleared up the whole subject by showing the nature of the distinction between what may now be called a true gas, and what may be called a true vapour. His experiments, on carbonic acid and other bodies, led to the experimental law that

There is a Critical Temperature for every vaporous or gaseous substance; such that, only when its temperature is below this, can the substance be reduced to the liquid form by any pressure, however great.

The critical temperature for sulphurous acid is high, and this substance is easily liquefied at ordinary temperatures by an atmosphere or two of pressure. That for carbonic acid is 30°.9 C., and it requires, at ordinary temperatures, forty or fifty atmospheres for its condensation. Water vapour has to be raised to a temperature of about 412° C. before it ceases to be condensable by pressure. On the other hand, the critical temperature for Hydrogen, Oxygen, Nitrogen, and Carbonic Oxide is so low that even considerable pressure requires to be assisted by the most powerful freezing mixtures before the liquefaction of these substances is accomplished. Cailletet and Pictet, separately but simultaneously, effected in the end of 1877 this complete verification of Andrews's law.

175. When a gaseous substance is at a temperature higher than its critical temperature, we may call it a true gas; when at a lower temperature, a true vapour. The distinction is well shown by the following brief account of Andrews's experiments on carbonic acid.

At $13^\circ.1$ C. carbonic acid gas was reduced by a pressure of forty-nine atmospheres, as measured by an air gauge, to $\frac{1}{81}$ of its original volume under one atmosphere, without undergoing any change of state. With a slight increase of pressure, liquefaction occurred, and the volume of the carbonic acid in the liquid state was $\frac{1}{463}$ of the original volume of the gas. During the process of liquefaction both liquid and gas were visible in the tube in which the experiment was made. After complete liquefaction, the carbonic acid continued sensibly to contract as the pressure was augmented. At $21^\circ{\cdot}5$ C., similar results were obtained, but liquefaction did not occur till a pressure of sixty atmospheres was reached. At $31^\circ{\cdot}1$ C., which is $0^\circ{\cdot}2$ above the critical temperature of carbonic acid, the gas behaved in the same way as at lower temperatures, till a pressure of seventy-four atmospheres was attained, when a further increase of pressure produced a very rapid, but nowhere abrupt, diminution of volume, unaccompanied by any evidence of liquefaction or of the presence (at any stage of the process) of two different states of matter in the experimental tube. After this the carbonic acid, now reduced to $\frac{1}{380}$ of its original volume, continued slowly to diminish in volume as the pressure was increased. At higher temperatures this rapid fall became less manifest, and at 48° it could no longer be observed. [This question will be more fully discussed in Chapter XX. below.]

176. For the formation of liquid water from ordinary vapour a nucleus of some kind must be present, else the vapour may remain in a state of saturation, sometimes even of supersaturation, without condensing. This has quite recently been shown by Aitken, who has traced the formation of clouds and fogs to the presence of excessively fine particles of dust in the air. These dust particles are found to be completely arrested by a plug of cotton-wool, through which air is made to pass. Each dust particle secures a share of the vapour, so that, when they are very numerous, the share of each is small, and a fog or mist is formed; when they are few each gets more, and clouds or even rain-drops are produced. The smaller the number of nuclei the larger are the individual rain-drops. Aitken concludes from his experiments that, if the atmosphere were entirely free from such particles no mists or clouds could be formed, no rain would fall, and the air would get rid of its superfluous moisture only by *direct* deposition upon bodies exposed to it.

177. *Résumé of* §§ 159-176. — Vaporisation. Dalton's Law. Regnault's Determination of the Pressure of Saturated Water-vapour at different temperatures. Hypsometric Thermometer. Total Heat of Steam. Freezing by Evaporation. Condensation. Dew-point. Hygrometers. Distinction between Gas and Vapour. Andrews's Critical Point. Cause of Clouds and Fogs.

CHAPTER X.

CHANGE OF TEMPERATURE. SPECIFIC HEAT.

178. Refer again to §§ 45-48. In these sections we have spoken of the gradual rise of temperature of water substance, as heat is steadily applied to it, in the solid, liquid, and gaseous forms, and the question immediately suggests itself: What amount of heat is required for each degree of rise of temperature by the substance in each of these three states? In other words, does water substance become easier to heat or harder to heat by being changed from one of the molecular states to another? Again, if a pound of water and a pound of mercury, at the same temperature, have equal quantities of heat communicated to them, will the heating effect be the same for both; or, if not, in what proportion will be their rise of temperature?

179. Experiment has answered these and other analogous questions, in a form which shows that bodies differ in a very marked manner as to this effect of heat; and we therefore define, as a property of each particular substance (under assigned conditions) what is called its *Specific Heat*, as follows :—

The specific heat of a substance, under any specified conditions, is the number of units of heat required, under these *conditions, to raise the temperature of one pound of the substance by 1° C.*

We have already defined a unit of heat as the amount of heat required to raise the temperature of a pound of water by 1° C.; it is therefore clear that, by our definition, the specific heat of water is 1. It will be seen later (§ 184) that the specific heat of water varies so slowly with temperature that it is practically the same at 0° C. and at 10° C., *i.e.* at 32° F. and at 50° F. (see § 55). The term Specific Heat was originally devised by the Calorists, but it is still used in science, like Latent Heat, Centrifugal Force, etc., etc., as it is convenient and quite harmless.

180. There are many experimental processes for determining Specific Heat, but we cannot spare space for more than two or three so far as solids and liquids, under ordinary pressures, are concerned. We commence with the most readily intelligible of them; a process, in fact, long ago devised by Black.

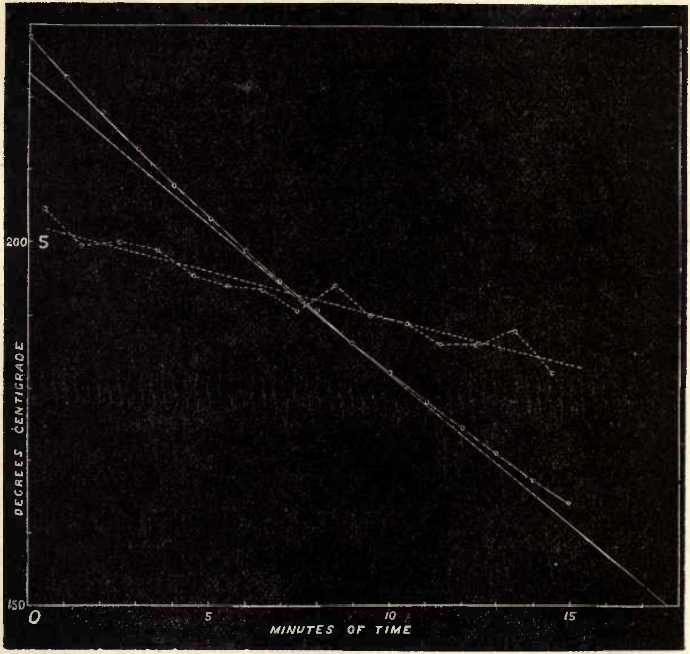
It will be found, when we are dealing with *Radiation*, that the quantity of heat radiated from the surface of a hot body, in a given time, depends (so far as the body itself is concerned) solely upon the *temperature* and the *nature of the surface.* Hence, if we take a thin shell of metal and fill it successively with different liquids, each at a temperature higher (or lower) than that of the surrounding bodies, we know that its rate of loss (or gain) of heat by radiation will be the same at any one temperature whatever be the substance which fills it. Suppose, for simplicity, that the shell holds just one pound of hot water. Then, if the bulb of a thermometer be plunged in the water we know that, for every degree the thermometer falls, one unit of heat has been removed from the water by radiation and convection. Let us note the number of seconds which elapse for each degree of temperature as the thermometer falls, and we may then construct a table of the number of seconds required for the loss of one unit of heat by radiation from the shell at each successive degree of temperature.

Now fill the shell with another hot liquid, mercury suppose. (To be thus employed the shell must be made of iron, for chemical reasons.) Note again the time required for each degree the thermometer sinks. It will be found to fall *faster* than when the contents were water; although, in consequence of the great specific gravity of mercury, there are 13·6 pounds of that liquid in the shell. In fact, the time of cooling through any given range of temperature is now less than half of what it was when the shell was filled with water. Hence we conclude that the specific heat of water is more than 27·2 times that of mercury, because the same change of temperature is produced in one pound of water and in 13·6 pounds of mercury, while the water loses more than twice as much heat as the mercury. The correct specific heat of mercury is found in this way to be about $\frac{1}{30}$ only.

181. The process we have just described is liable to several objections. The most serious of these are (1) that the contents of the shell cannot, unless constantly stirred, have the same temperature throughout; (2) that, unless the neck of the shell be closed, there is serious loss of heat by evaporation—a loss which is of greatly different amounts with different liquids at the same temperature.

But for the beginner in experimental science, the process is very instructive; especially if he employs a *graphic method* in deducing the results. We may take this opportunity of giving a general notion of this most important process. Although from its very nature it cannot pretend to any great accuracy, it is always free from *large* error; and is therefore an almost indispensable auxiliary to numerical calculation, in which the most expert calculators may make serious mistakes.

[Thus, suppose the results of the observations of temperature in terms of the time, as furnished by the readings of

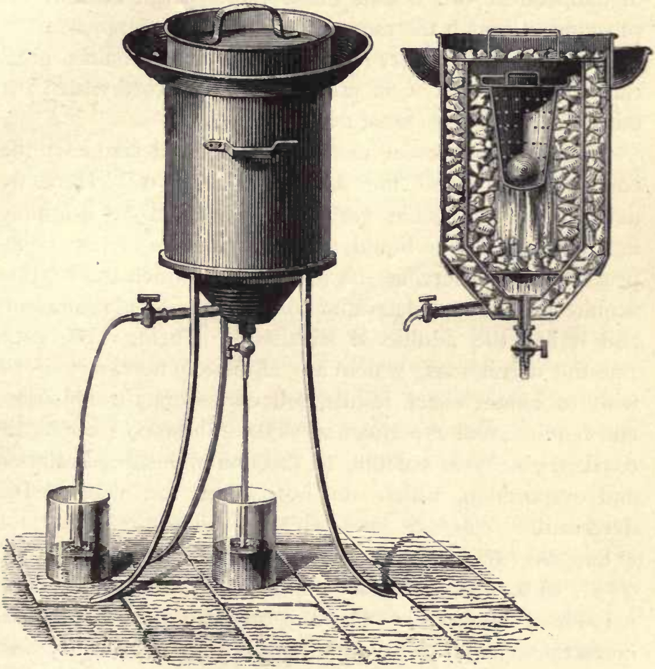


the thermometer after the lapse of successive intervals, equal or not, be plotted (on mechanically ruled paper) as above; intervals of time being measured horizontally, corresponding temperatures vertically. The figure represents, on a much reduced scale, the original plotting of the data of part of an actual experiment; the cooling of the short bar in Forbes's method for measuring thermal conductivity (Chapter XIV. below). The horizontal line is divided into minutes of time, the vertical line (on its left side) into degrees centigrade. Suppose a smooth curve to be drawn *liberâ manu* (the full curve in the figure), so as to agree as nearly as possible with the observed points. This curve will represent an approximation (the more close the shorter are the intervals between the observations) to that which would have been obtained by the continuous photographic process of § 136. Then if *rate of cooling* at any temperature, say 186°, be required, all that has to be done is to draw a horizontal line through 186° on the scale of temperatures, and where this line meets the curve *draw a tangent*, producing it both ways to meet the two divided lines. As drawn, it cuts off 73° on the temperature scale, and $17^{m}\cdot6$ on the time scale. Hence the rate of cooling at 186° is 73° in $17^{m}\cdot6$, or $4^{\circ}\cdot15$ per minute.

Even the best mercury thermometers, when the column is rising or falling otherwise than *very slowly*, are found to move occasionally by sudden starts, the surface film sticking for a moment in the tube and thus subjecting the column to pressure or tension. It is possible also that the bulb recovers by starts from its state of dilatation. Hence for the purpose of finding *rates* of cooling, as in the case above, it is sometimes better to make the observations of temperature at successive equal intervals taken as the unit of time, and to plot the *differences* of the successive readings midway between the beginning and end of the interval in question. In the figure the corresponding points are put in and connected by *dotted* lines. The time scale is the same as before, but the degrees on the temperature scale are ten times as long as before. Its numbers are inserted on the *right* side of the temperature scale. We now find it impossible to draw a *smooth* curve through the various points, but if we draw a smooth curve (the dotted one in the figure) which (perhaps not passing through any of them) shall show on the whole as much divergence of observed points from itself on one side as on the other, the ordinates of this curve will be *themselves* the rates of cooling required, and no drawing of tangents will be necessary. In the figure, the ordinate of this dotted curve, corresponding to 186°, is 4°·12, thus agreeing within one per cent. with the result of the former method. Experience alone can guide us, in any case, as to which of these methods is to be preferred.]

182. Another method of determining specific heat is supplied by the ice-calorimeter, in which the amount of heat lost by a hot body in cooling to 0° C. is measured by the amount of ice which it melts. The general principle on which the calorimeter is constructed will be obvious from the figure. There are virtually three vessels, one within another, the two outermost containing ice and water at ordinary atmospheric pressure, and therefore always at 0° C. The middle vessel can part with no heat to the outer one unless its temperature changes; but this cannot be until all its contained ice is melted (§ 142). We have thus a very simple and fairly effective method of preventing loss of heat. Into the interior vessel the substance whose specific heat is to be measured is dropped, at a known temperature, and the whole is closed up. After a short time the whole contents of the vessel are again at 0° C., but *the heat disengaged from the substance has melted some of the ice in the middle vessel.* In the older and rougher forms of the instrument, as designed by Lavoisier and Laplace (from

one of which the sketch is taken), the amount of ice melted was given by the amount of water which drained away from the middle vessel. Of course there was considerable error, as some of the water was necessarily retained by capillary



forces. In the improved form, as designed by Bunsen and others, the middle vessel is *filled* with solid ice to begin with, and the amount melted is calculated from the *diminution of the volume* (§ 145) *of the contents*, as shown by an external gauge containing mercury in contact with the ice.

The result of each experiment shows (§ 151) the number of units of heat lost by a known mass of a substance in passing from a known temperature to 0° C. By dividing the number of units of heat lost by the number of pounds of the substance and by the number of degrees of change of temperature, we obtain the *Average Specific Heat* of the substance through the range of temperature employed.

This method is very troublesome, and requires great care and skill; but it is much more trustworthy than any other, when properly conducted.

183. The only other method we need describe is the common one called the *Method of Mixture.* Here we determine the specific heat of a substance by dropping it, when hot, into a liquid (usually water) at a lower temperature, and observing the temperature which the mixture acquires. For rough determinations this process is sufficient, and it has the additional advantage of being very easy. But the corrections, which are absolutely necessary if we wish to obtain exact results, are exceedingly troublesome and require great experimental skill. These corrections are required chiefly on account of the loss of heat by radiation and evaporation, which do not affect the method last described.

Suppose M pounds of one substance, at temperature T° C., to be mixed with m pounds of another substance at a lower temperature, t° C.; and suppose the mixture (all corrections made) to have the temperature τ° C., which must obviously be intermediate between T and t. Then *the heat lost by the one substance has gone to the other.* If the specific heats of the two substances be S and s respectively, the loss of the first (in units of heat) is

$$M S \, (T - \tau).$$

The gain of the other is (in the same units)

$$m\,s\,(\tau - t)$$

Equating these quantities, we find at once

$$\frac{S}{s} = \frac{m\,(\tau - t)}{M\,(T - \tau)},$$

which gives the *ratio* of the specific heats; or, if the second substance be water, the specific heat of the first substance. [It is to be observed that S is the *average* specific heat of M from T to τ, s that of m from τ to t.]

It is well to observe that the temperature of the mixture, if no heat be lost by radiation or evaporation, is

$$\tau = \frac{M\,S\,T + m\,s\,t}{M\,S \;+\; m\,s}.$$

The quantities MS, ms, which appear in this expression, are called *Water-equivalents* of the substances. The water. equivalent of any mass is thus the number of pounds of water which would be altered in temperature to the same extent, by the same number of units of heat, as the given mass.

[And we see that the temperature of a mixture is given in terms of the water-equivalents of the several substances and their several temperatures, by a formula exactly the same as that which gives the position of the centre of inertia of a number of particles in one line, in terms of their separate masses and positions.]

Another term which is sometimes of use, is the *thermal capacity* of a substance. This may be regarded as the water-equivalent of unit volume of the substance, and its numerical value is obviously the product of the density by the specific heat of the substance. (See § 249).

184. We will now give some general notions as to relative specific heats of solids and liquids. But before doing so, it is well to remark that, in general, specific heat rises with temperature; and that (as above stated) our experimental determinations give directly the *average specific heat* of a substance through a certain range of temperature. From the results of such determinations, however, if they be sufficiently numerous and varied in their circumstances, it is not difficult to deduce the true specific heat as a function of the temperature.

According to Regnault, a pound of water at 0° C. requires 100·5 units of heat to raise it to 100° C., and 203·2 units to raise it to 200° C.

These are represented by the formula

$$H = t + 0·000,02\, t^2 + 0·000,000,3\, t^3,$$

which gives, for the specific heat of water at any temperature, t° C., the expression

$$1 + 0·000,04\, t + 0·000,000,9\, t^2.$$

Thus the change for any ordinary ranges of temperature is extremely small. Refer again to § 61.

The specific heat of ice at 0° C. is almost exactly *half* that of water. Regnault has shown that it diminishes as the temperature is lowered.

That of glass may be roughly assumed as about 0·2. That of platinum is about 0·0355, and varies very slightly even for large ranges of temperature. With other metals, such as copper, the increase of specific heat is (roughly) about 10 *p. c.* for 100° C. It appears to be rather more in iron. But we have no very exact knowledge on this subject, as different specimens seem to give very different results.

SPECIFIC HEAT OF ELEMENTARY SOLIDS.

Lead	0·031	207	6·4
Tin	0·056	118	6·6
Copper	0·095	63·5	6·0
Iron	0·114	56	6·4
Sodium	0·293	23	6·7
Lithium	0·941	7	6·6

The first column of the table gives the specific heat at ordinary temperatures, the second the *atomic weight* of the substance. The numbers in the third column are the products of those in the first and second. It will be seen that the numbers in this third column are within about 10 per cent. of one another. Hence it is concluded that *the specific heat of an elementary solid is inversely as its atomic weight.* The small differences in the last column are attributed (in part at least) to the known fact that the specific heat of each substance increases as the temperature rises, and therefore that, as these specific heats are measured all at the same temperature, the different bodies compared are taken in different physical states, some being much more nearly at their melting-point than others.

It is probable that very important information as to the nature of matter will be obtained from this experimental fact. Perhaps its value may be more easily seen if (by § 183) we put it in the form :—

The atomic water-equivalent is nearly the same for all elementary solids.

A similar law has been found to hold for groups of compound bodies of *similar atomic composition.* But the product of the specific heat and the atomic weight varies in general from group to group of such compounds.

185. In general, as we have seen, the specific heat of a

substance in the liquid state is greater than in the solid state.

SPECIFIC HEATS OF ELEMENTARY LIQUIDS.

Lead	0·040	400° C.
Tin	0·064	300° C.
Mercury	0·033	30° C.

The second column gives the mean temperature of the range through which the specific heat is measured.

The specific heat of Alcohol, which it is important to keep in mind, is (at 30° C.) a little above 0·6.

186. In the case of gases the problem of determination of specific heat is not only more difficult, from the experimental point of view, than in the case of a solid or of a liquid, but it is also more complex from a theoretical point of view. For, in consequence of the great expansibility of gases, we have to specify the conditions under which the measurement is to be made. Thus the gas may be maintained at the *same volume*, or at the *same pressure*, throughout the range of temperature employed. And we therefore speak of the *Specific Heat at constant volume*, or of the *Specific Heat at constant pressure.* Thermo-dynamics gives us a simple relation between these quantities for the ideal perfect gas (§ 126); and therefore for gases such as Air, Hydrogen, &c., it is only necessary to determine directly one of the two specific heats. This is a very happy circumstance, because the experimental difficulties of determining the specific heat at constant volume are extremely great. The mass of a gas at ordinary pressures is small compared with that of the containing vessel, unless the vessel be of unwieldy dimensions; and we cannot get over this difficulty by compressing the gas, for we must then make the vessel strong (and therefore massive) in proportion.

The measurement of the specific heat at constant pressure is effected by passing the gas, at a uniform rate, through two spiral tubes in succession. In the first of these it is heated to a known temperature, and in the second it gives up its heat to a mass of water in a calorimeter in which that spiral is immersed. From the volume of the gas which has passed through the spirals, we can calculate its mass, and the observed rise of temperature in the water of the calorimeter supplies the requisite additional datum.

This process was devised by De la Roche and Bérard, but its details were greatly improved by Regnault.

Further remarks on this subject, especially from the theoretical point of view, must be deferred for the present.

187. Regnault's experiments showed that, for gases like air, the specific heat of a given mass of the gas is independent of the temperature and pressure, and therefore (§ 124) of the volume.

Hence the specific heat of a given volume of such a gas varies directly as the density.

Equal volumes of different gases of this class, at the same pressure, have approximately equal specific heats.

SPECIFIC HEATS AT CONSTANT PRESSURE.

Air	0·237	Oxygen	0·217
Nitrogen	0·244	Hydrogen	3·409

It will be seen that these numbers are very nearly in the inverse ratio of the densities of the various gases (see § 184).

Experiments on sound (§ 397) have shown that the ratio of the two specific heats of air is about 1·408, whence we see that the specific heat of air at constant volume is 0·168.

The specific heat of water-vapour under the same condition is 0·48, a little less than that of ice (§ 184). Hence water-substance has twice as great a specific heat in the liquid state as in the solid or in the vaporous state.

188. *Résumé* of §§ 178–187.—Change of temperature of unit mass by a given quantity of heat. Specific Heat. Method of Cooling. [Digression on Graphic Methods.] Ice Calorimeter. Method of Mixtures. Water Equivalent. Thermal Capacity. Relation between Specific Heat and Atomic Weight. Specific Heat of Gases: (*a*) at constant volume, (*b*) at constant pressure. Specific Heat of Water-vapour.

CHAPTER XI.

THERMO-ELECTRICITY.

189. We have already stated, in § 49, the fundamental fact of Thermo-electricity as discovered by Seebeck; and we now propose to examine the subject more closely from the experimental point of view. For this purpose we must use the term *Electro-motive Force.* So far as we require its properties they may be enunciated as follows:—

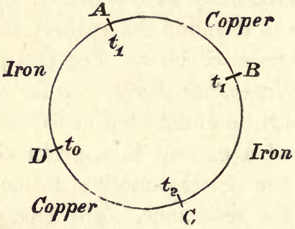
The strength of a current in a given circuit is directly proportional to the Electro-motive Force, and inversely proportional to the resistance. The energy of the current is the product of the Electro-motive Force (contracted as *E.M.F.*) and the strength of the current.

It will be advantageous to commence with the following statement of an experimental result:—

If e *be the E.M.F. in a thermo-electric circuit when* t_0 *and* t_1 *are the temperatures of the junctions; and* e' *the E.M.F. when the temperatures are* t_1 *and* t_2*; then when the temperatures are* t_0 *and* t_2 *the E.M.F. is* $e+e'$.

[Consider this from the point of view given by the following figure; where the circuit is supposed to consist of *four* wires, alternately of two metals (say iron and copper). See, again, § 49, where it is stated that the wires may be *soldered* together at the junctions. No third substance, such as metal or solder, introduced into the solid circuit, is found to affect the result if it have the same temperature at the points where it meets each of the two metals.

Let the temperatures of the four junctions be as in the figure. Then D and A together (if B and C had the same temperature with one another) would give *E.M.F.* e, and B and C together (if D and A had one common temperature) would give *E.M.F.* e'. Hence as the figure is drawn, there would be total *E.M.F.* $e + e'$, provided the assumptions made (in brackets) above were superfluous.



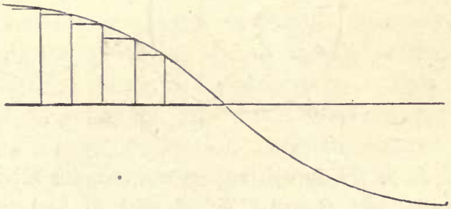
But the *E.M.F.* may be looked upon as due entirely to the difference of temperatures of C and D, for the temperatures of A and B are equal, and therefore the copper wire $A\ B$ produces no effect. Hence the contribution of each metal to the whole *E.M.F.* of such a circuit depends only on the temperatures of its ends, *i.e.* is independent of the temperature of the rest of the circuit.]

190. It follows from the experimental fact above, that we may break up any interval of temperature, t_0 to t_n, into ranges:—viz. t_0 to t_1, t_1 to t_2, &c., t_{n-1} to t_n; and the *E.M.F.* in a simple circuit of two metals, when the junctions

are at t_0 and t_n will be the sum of its separate values when the junctions are successively at t_0 and t_1, t_1 and t_2, &c, and t_{n-1} and t_n.

We shall now look upon these as successive equal ranges of temperature, and we shall define the *thermo-electric power* of a circuit of two metals, at mean temperature t, as the *E.M.F.* which is produced when one junction is kept half a degree above, the other half a degree below, t.

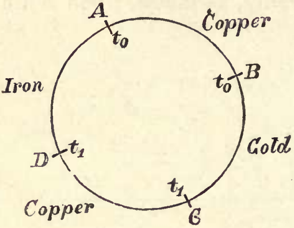
We thus get the means of representing in a diagram the relative thermo-electric positions of any two metals at different temperatures. Thus we may erect little rectangles one degree in breadth, as below, upon a line representing one of the metals.



The area of each rectangle is the thermo-electric power corresponding to the temperature at the middle of its base; and, by taking the intervals of temperature small enough, it is obvious that the final upper boundary of the group of rectangles will become a continuous line. This will represent at every point the relative thermo-electric situation of the second metal with regard to the first, as the first is represented by the line on which temperatures are measured. And the sum of any number of the rectangles (giving the *E.M.F.* for any two assigned temperatures of the junctions) is now represented by the area of the corresponding portion of the curve.

191. But there is a much more general experimental result than that in § 189. *At every temperature the algebraic sum of the thermo-electric powers of metals* α *and* β, *and* β *and* γ, *is the thermo-electric power of* α *and* γ.

[Suppose *one* of the iron wires in the diagram of § 189 to be replaced by a third metal, say gold; and let the temperatures of the ends of one of the copper wires be t_0, and of the other t_1. Then *A* and *D* (if *B* and *C* had the same temperature) would give *E. M. F.* depending on iron-copper alone at the temperatures t_0, t_1; *B* and *C* (if *A* and *D* had the same temperature), would give *E. M. F.* due to a copper-gold circuit with its junctions at the same two temperatures. It is easy to see, as before, that the experimental result shows the assumptions (in brackets) to be superfluous. For, as the ends of each copper wire are at the same temperature, the circuit acts as one of iron-gold alone, its junctions also having the temperatures t_0, t_1.]



Thus if, by the process of § 190, we form the lines representing the positions of iron and of gold, each with regard to copper taken as the standard, the lines so drawn will show the position of iron and gold relatively to one another. Hence the possibility of constructing a *Thermo-electric Diagram* containing a single line for each metal. The idea of such a representation was suggested by W. Thomson in 1855, and he gave a rough preliminary sketch of it. A "first approximation" to an accurate diagram was given by Tait in 1873. This is reproduced on a small scale in § 198, but it cannot be fully explained until some additional experimental facts are stated. It will then be found that a properly drawn thermo-electric diagram embodies all that is known about the subject of thermo-electricity. And thus, by the use of the diagram, we are now able to present the subject in a much more simple and connected manner than was formerly possible.

192. The electric current in a thermo-electric circuit represents a certain (usually very small) amount of energy, whose measure as before stated is the product of the *E.M.F.* by the strength of the current. This can have no other source than the heat which has been given (as in § 49) to a part of the circuit. And the existence of the current implies a loss of heat by the circuit as a whole.

It is a very remarkable fact in the history of science that, without any reference to the theory of energy, Peltier (1834) discovered by experiment that—

When a current of electricity from an external source passes through a junction of two metals, it causes an absorption or a disengagement of heat.

If the direction of the current be the same as that of the current which would be produced by heating the junction, the effect is absorption; and vice versâ.

This is very easily proved by the help of a galvanometer. Two wires (say iron and copper) are brazed together at their middle points only; one of the free ends of the iron is maintained in connection with one pole of a single voltaic cell, the other end is in connection with one of the ends of a galvanometer coil. The copper wire is so arranged that by rocking it over to one side we close the circuit of the cell, leaving the galvanometer circuit open; and by rocking to the other side we break the battery circuit and close the circuit of the galvanometer; the iron-copper junction being thus alternately in one circuit and in the other. There is always a deflection of the galvanometer after the voltaic current has traversed the junction. And it changes sign when the direction of that current is reversed.

The wires used for this experiment should be stout, else the heat generated in the circuit by ordinary resistance to the battery current may be greater than the Peltier effect which is sought.

When proper precautions of this kind are taken, a notable amount of heat may be produced or absorbed. Lenz, in 1838, succeeded in freezing a little water by passing a current of electricity in the proper direction through a bismuth-antimony junction, the metals themselves being surrounded by melting snow.

The direct quantitative measurement of the Peltier effect, *at different temperatures*, presents very great experimental difficulties. These have been only partially overcome as yet, mainly by the experiments of Naccari and Bellati. The results agree, as well as could be expected, with those stated below. There can be no doubt, however, that for any one pair of metals, kept at a given temperature, the Peltier effect is directly proportional to the strength of the current employed.

193. It was Joule who first remarked that the Peltier phenomenon furnishes a clue to the source of the energy

of a thermo-electric current; and it is quite possible that there *may be* pairs of metals (more probably alloys) for whose circuits it is the *only* source of the current. [This will be seen in § 199 below.]

But a phenomenon, noticed by Cumming very soon after the publication of Seebeck's discovery, shows that the Peltier effect is in general a part only of the source of the current. This discovery of Cumming's may be stated as follows:—

In certain circuits, such as those of iron-copper, iron-silver, iron-gold, etc., if one junction be kept at ordinary temperatures, and the temperature of the other be steadily raised, the E.M.F. increases more and more slowly till it reaches a maximum, then gradually diminishes, and finally is reversed.

Sir W. Thomson explained this effect as follows:—At that temperature of the hot junction for which the *E.M.F.* is a *maximum* (in Cumming's experiment), the two metals are neutral to one another, *i.e.* their thermo-electric power vanishes, *and the Peltier effect also.* This occurs, as the figure in § 190 shows, when the lines representing them intersect; for, after the intersection, the rectangles (from which the figure was composed) are turned the opposite way, and must therefore have the opposite algebraic sign.

He proceeds to reason thus:—Suppose a copper-iron circuit, in which the hot junction is at the neutral temperature, and the other at any lower temperature: we cannot suppose the energy of the current to come from the heat of the hot junction: for, as the metals are there neutral to one another, the Peltier effect must be *nil.* Also the cold junction is *heated*, not cooled, by the current. Hence the energy can only come from one or other, or both, of the wires themselves, and it must come from them in virtue of the differences of temperatures of their ends. The assumption that the Peltier effect vanishes at the neutral temperature requires experimental proof, which has as yet been only partially furnished. We merely mention this to show that the experimental basis of the reasoning is not quite complete. Campbell (*Proc. R.S.E.* 1882) has to a certain extent supplied a *qualitative* verification, by showing that the ratio of the Peltier effects at two temperatures is consistent with that deduced from the thermo-electric diagram. It is probable that by his method the vanishing of the Peltier effect at the neutral point may be experimentally established.

Thus Thomson was led to the conclusion that:

An electric current in an unequally heated conductor, of one at least of two metals which have a neutral point, must produce absorption, or disengagement, of heat, according as it passes from hot parts to cold, or vice versâ.

After a series of elaborate experiments (described in the *Phil. Trans.* for 1855) Thomson found that:—

When the current passes from cold to hot in copper there is absorption of heat, and vice versâ. In iron the effects are the opposite.

This "Thomson effect" is sometimes called *Electric Convection of Heat.* As will be seen later (§ 199), the above statement, so far as iron is concerned, requires modification at very high temperatures.

194. Thus, Thomson speaks of the specific heat of vitreous electricity in a metal; and regards it as positive in copper and negative in iron, in consequence of the difference of behaviour just explained. Thomson gave, along with these remarkable results, the thermo-dynamical theory of the thermo-electric circuit in terms of Peltier effect and electric convection, but without assigning a special expres-

sion for the amount of convection or of the Peltier effect in terms of temperature. In fact, he says that the lines representing various metals, in the thermo-electric diagram, "will generally be curves." But he showed experimentally that the thermo-electric current, in a circuit of two metals, vanishes not only when the junctions have the same temperature (as in § 190), but also when their temperatures are equidistant from that of their neutral point. When one of the metals is represented by a straight line (as in the diagram of § 190) the other is therefore represented by a curve which crosses it at the neutral point, and has *the same form and dimensions* on opposite sides of that point.

[The rest of the chapter is, for the most part, taken from the *Rede Lecture* for 1873.*]

It has been found, by measurements of the *E. M. F.* of numerous pairs of metals through the whole range of mercury thermometers, that if the thermo-electric position of any one metal be represented by a straight line on the diagram, the lines for other metals are (in general) also straight. This involves no assumption other than that just named. So that whatever may ultimately be found to be the rigorous expression for electric convection of heat in terms of temperature, and therefore the true form of the thermo-electric diagram, we may assert that if the diagram be so distorted (by shearing) that the line of any one metal (except iron, &c., §§ 198, 199) becomes straight, those of the great majority of other metals will also become straight. From this it follows that *the rate at which the thermo-electric power of two metals changes with temperature is constant.*

195. Thomson's theoretical expressions, just alluded to, are based on the supposition that there is no reversible

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* *Nature*, vol. viii. pp. 86 and 122.

thermal effect in the circuit but the Peltier and Thomson effects. If this be so, it follows from the *theory* of heat and the result just given (as will be shown in Chapter XXI.), that the Peltier effect is proportional to the thermo-electric power and to the absolute temperature. Also the (algebraic) difference of the specific heats of electricity in the two metals is proportional to the absolute temperature.

Hence, if there be a metal which has no specific heat of electricity at any temperature, it follows by theory from the above experimental result (§ 194) that:

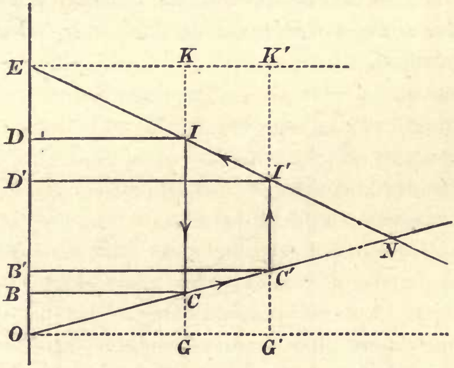
The specific heat of electricity in a metal is in general directly proportional to the absolute temperature.

Le Roux, in 1867, made a valuable series of direct measurements of the electric convection of heat, and showed that it is null, or at least exceedingly small, in lead.

196. We are now in a position to explain the indications of the thermo-electric diagram, and to use it for the calculation of the Peltier and Thomson effects, showing fully whence the energy of the thermo-electric current is derived.

Let the cut represent a part of the diagram, two metals (copper and iron, suppose) being represented by the straight lines CC' and II'. The vertical axis $O\ E$ corresponds to the absolute zero of temperature. Draw lines parallel to $O\ E$, corresponding to t and t', the (absolute) temperatures of the two junctions, and cutting the lines of the metals in C, I, and C', I', respectively. Also (for simplicity) suppose both of these temperatures to be lower than that of the neutral point *N.* Then the *E.M.F.* of the copper-iron circuit is (§ 190) represented by the area $C\ C'\ I'\ I$; and, as the figure is drawn, it produces a current going round the circuit in the *positive* direction as shown by the arrows, passing from copper to iron at the hotter junction. [The reason why the line of copper has been drawn so as to *rise* towards the right, is the fact of its specific heat of electricity being positive (§ 194).] This area *C C′ I′ I* will represent the amount of energy of the current, if it be made unit by properly adjusting the resistance of the circuit.

Now (by § 195) the area *D′ B′ C′ I′* represents the Peltier effect (absorption of heat) at the hot junction if unit current were passing through it; and *D I C B* the Peltier effect (development of heat) at the cold junction under the same

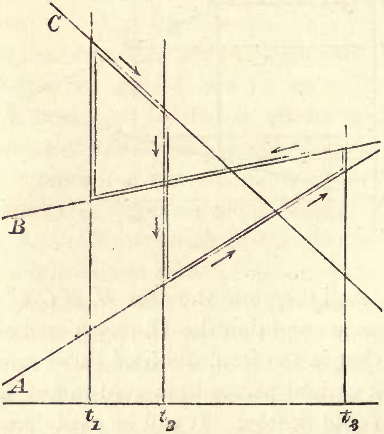


condition. And therefore the area *B′ B C C′* will represent under the same condition the Thomson effect in the copper, *D D′ I′ I* that in the iron. Both of these represent absorption, for the current passes from cold to hot in copper, and from hot to cold in iron. It will be easily seen (by Euclid) that *G C* is the specific heat of electricity in copper at $t°$ *C.* (positive) while *K I* (negative) is that in iron.

For the whole area *B C C′ I′ I D* may be taken to represent energy taken in, in the form of heat; while the part

$D\ I\ C\ B$ represents energy given out in that form. The difference, $C\ C'\ I'\ I$, remains for the production of the thermo-electric current. Thus the first law of thermodynamics is satisfied. In order to make these representations *exact*, instead of merely *proportional*, each area must be multiplied by the strength of the current actually passing in the circuit.

To show that the second law applies, the algebraic sum of all the portions of heat taken in and given out, each divided by the absolute temperature at which the operation takes place, must be proved to vanish. But we have obviously $B'D' - BD + BB' + D'D = 0$, which proves the proposition.



[It will be good practice for the student to work out the corresponding diagrams, when one or both junctions are above the neutral point; and when both metals have positive specific heats of electricity. Also to treat the case of a circuit of three metals in which the three junctions are at different temperatures. We insert a sketch for this case. Here A and B have their specific heat of electricity positive, C negative. The junction B, C, is at t_1, C, A, at t_2, and A, B, at t_3; and the area bounded by the doubled line (partly positive, partly negative) represents the *E.M.F.*]

197. Let us now consider how the strength of the current ought to vary with the temperatures of the junctions if these statements be correct. [First figure in last section].

In other words, if CI be fixed, how does the area $CC'I'I$ vary as the temperature t' increases?

Without introducing symbols we may easily answer the question thus:—Let $C'I'$ represent velocity, and t' time. Then the area $CC'I'I$ represents the space described in the time $t'-t$. But evidently the velocity diminishes uniformly as the time increases; *i.e.* it is a case of *uniform acceleration* vertically downwards, associated with uniform velocity to the right; exactly the case of an unresisted projectile. Hence:—When one junction of a thermo-electric circuit is kept at a constant temperature, and the temperature of the other is gradually raised, the curve representing the strength of the current in terms of the variable temperature is a parabola, whose axis is parallel to that of *E.M.F.*, and the abscissa of whose vertex is the temperature of the neutral point.

This has been observed to be very accurately the case with the majority of thermo-electric pairs; but it is not the case for all ranges of temperature when iron, or nickel, is one of the two metals.

[An erroneous explanation of thermo-electric currents, probably suggested by this experimental fact, but based upon the assumption that the source of the *E.M.F.* of a circuit of two metals lies entirely in the junctions, was given by Akin in 1863,[1] and shortly afterwards by Avenarius.[2] As this explanation has already found its way into some text-books, it is necessary to direct the reader's attention to the fact that it cannot possibly be correct. Among other defects it ignores entirely the existence of the Thomson effect, which has been thoroughly established as a *vera causa* by independent experimenters.]

198. The thermo-electric diagram opposite (from *Trans. R. S. E.*, 1873) contains the lines of a number of common metals for a range of temperatures such as can be measured by mercury thermometers. Bismuth and antimony cannot be shown in it. The line of the latter lies high above its limits, that of the former considerably below them.

In consequence of the result obtained by Le Roux (§ 195) the line for lead has been adopted as the axis of abscissæ—along which temperatures are measured.

An auxiliary circuit of two alloys of iridium and platinum was employed in constructing the diagram. The specific heat of electricity is exceedingly small in each; but it must exist in one of them at least, for they have a neutral point somewhere about a low white-heat. But the explanations which we have just given show that for an extended range of temperature the *E.M.F.* of a circuit of these alloys must vary very nearly as the difference of absolute temperatures of the junctions. Such a combination forms an extremely convenient substitute for a thermometer, when great accuracy is not required; and it was indispensable for the investigation of the peculiar form of the iron line at high temperatures, which will presently be described.

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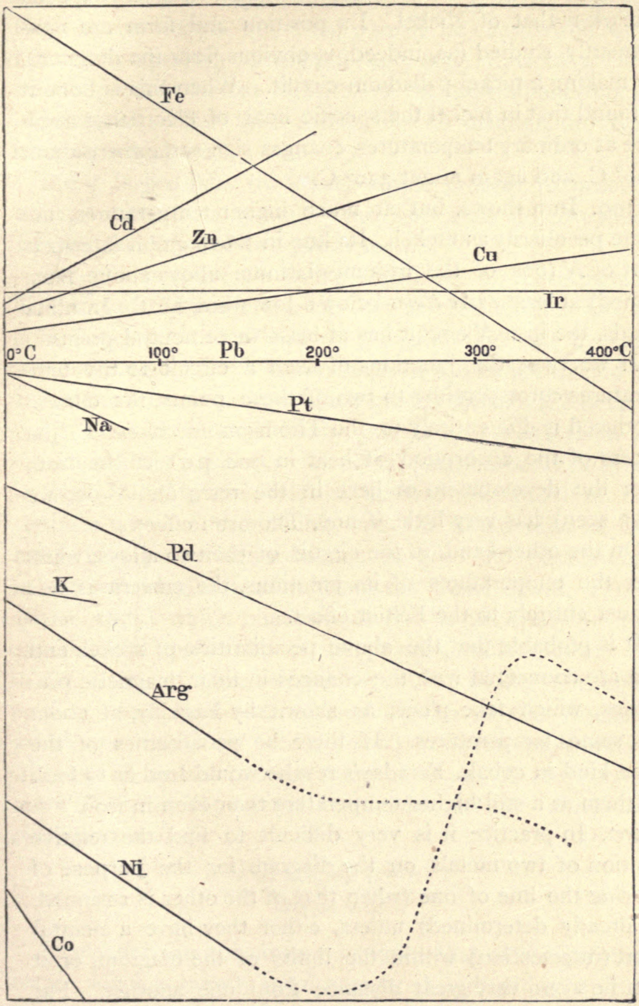
[1] *Proc. R. S.*, vol. xii., and *Camb. Phil. Trans.*

[2] *Pogg. Ann.*, 119.


Fe
Cd
Zn
Cu
Ir
0° C
100°
Pb
200°
300°
400°C
Pt
Na
Pd
K
Arg
Ni
Co

The only line in the diagram which calls for special remark is that of Nickel. Its position and form are conveniently studied (as, indeed, is obvious from the diagram), by making a nickel-palladium circuit. When this is done it is found that in nickel the specific heat of electricity, negative at ordinary temperatures, changes sign somewhere about 200° C. and again about 320° C.

199. Iron shows, but at much higher temperatures, the same peculiarity as nickel. Its line in the diagram intersects that of N (one of the iridium-platinum alloys above mentioned) at least *three times* below a low white-heat. In other words, the iron-N circuit has at least three neutral points.

If we raise the junctions of such a circuit to the temperatures corresponding to two of these points, the current produced is due entirely to the Thomson effect, *i.e.* to the excess of the absorption of heat in one part of the iron, over the development of heat in the rest; for N (as we have seen) has very little, if any, Thomson effect.

On the other hand, in the circuit of the two alloys, whatever the temperatures of its junctions, the current is due almost entirely to the Peltier effect.

It is probable that the above peculiarities of nickel and iron are connected with the changes in their magnetic properties, which take place, as shown by Faraday, at about the same temperatures. If there be peculiarities of the same kind in cobalt, Faraday's results would lead us to look for them at a still higher temperature than even in iron.

200. In practice it is very difficult to find the relative position of two metals on the diagram for the purpose of drawing the line of one (when that of the other is assumed, or already determined) unless, either they have a neutral point (intersection) within the limits of the diagram, or at least lie at no very great distance from one another. For

when they are far apart, the *changes* of *E.M.F.*, however large in themselves, are usually small in comparison with the whole quantity measured, and may thus to a considerable extent be lost sight of in the inevitable errors of observation. The lines shown in the diagram are very irregularly scattered.

But it is possible, by a very simple process, to procure what is virtually a metal whose line shall lie anywhere *between* the lines of two given metals.

For this purpose we use a *double arc* of these metals. This is made by soldering together at their ends a wire of gold (suppose) and a wire of platinum laid side by side without contact; and this combination will (when treated as a single wire) have a line which passes through the neutral point of gold and platinum, and lies between them in thermo-electric position. Its actual position between them is determined by the relative electric resistances of the separate wires of the double arc. It would take us too much into pure electric science to give the calculation: so the following statement (from the *Camb. Math. Tripos Exam.* 1875), which contains all that is necessary for the experimental application of the process, must suffice.

Let wires of three metals A, B, C, *having resistances* a, b, c, *have their ends soldered together at two junctions which are maintained at* (*different*) *constant temperatures. Then if* I_a *be the current when* A *is cut*, I_b *the current when* B *is cut, the current in* C *when all the wires are continuous will be*

$$\frac{a\,(b+c)\,I_a + b\,(c+a)\,I_b}{bc+ca+ab}$$

In practice the resistance c includes that of the galvanometer, which is usually large compared with either a or b;

and then the above formula takes the sufficiently approximate and exceedingly simple form

$$\frac{aI_a + bI_b}{a + b}$$

By the use of this artifice we can fill up all the gaps in the diagram.

201. To conclude this part of the subject, we give a brief table of approximate thermo-electric data for some common metals. These show how to draw the lines on the diagram, between the limits 0° and 350° C. Different specimens of the same metal do not agree very closely, so that the numbers are given on the same terms as are those in §§ 104, 153, &c.

NEUTRAL POINTS WITH LEAD.

Ni	(−424°)	Ag	−144°	Sn	+75°	Sb	−156°
Au	(−276)	Cu	−132	Ru	+136	Pb	. . . .
Arg	−238	Zn	−95	Al	+212	Rd	+132
Co	−228	Cd	−59	Mg	+239	Ir	∞
Pd	−172	Pt	−56	Fe	+356	Bi	(−580)

[*The numbers in parentheses are not, of course, temperatures.*]

SPECIFIC HEAT OF ELECTRICITY.

Fe	− ·00247	Au	+ ·00052
Pt (soft)	− ·00056	Cu	+ ·00048
Ir	− ·00000	Pb	·00000
Mg	− ·00048	Sn	+ ·00028
Arg	− ·00260	Pd	− ·00182
Cd	+ ·00218	Ni (to 175° C.)	− ·00260
Zn	+ ·00122	Ni (250°—310° C.)	+ ·01225
Ag	+ ·00076	Ni (from 340° C.)	− ·00180
Ru	− ·00106	Rd	− ·00058
Sb	+ ·01140	Bi	− ·0055
Co	− ·00585	Al	+ ·0002

The quantities in this last table are to be multiplied by the absolute temperature C. The unit employed corresponds to about 10^{-5} of the *E.M.F.* of a single Grove's cell. This is adopted because it enables the reader to form an idea of the extreme feebleness of the thermo-electric currents in general. The mode of calculating the *E.M.F.* of a circuit of two metals will be given later, when we discuss the thermo-dynamic theory of the circuit.

202. So far, we have considered the wires employed to be each of the same material and section throughout. Magnus long ago showed that differences of section in the circuit, or in any parts of it, had no effect on the *E.M.F.* [This is not necessarily true when the variation of section is so abrupt that there can be finite difference of temperature within a range comparable with that of molecular force.] But it has been found that hammering, knotting, twisting, and stress in general, applied to *one part* of a circuit of one metal only, makes it capable of giving thermo-electric currents when irregularly heated. The altered parts of the circuit behave to the unaltered parts as if they were of a different metal. In iron, nickel, &c., such effects can be produced by *magnetising* part of the wires. Also it has been found that if the two ends of a wire are at different temperatures, and be brought into contact, a current (of very short duration) is produced.

203. *Résumé* of §§ 189–202. General experimental properties of thermo-electric circuits. Consequences. Thermo-electric power defined. Peltier Effect. Neutral Point. Thomson Effect. Specific heat of Electricity in a metal. Thermo-electric diagram. How it represents *E.M.F.*, and the Peltier and Thomson effects. Mode of constructing the diagram experimentally. Anomalous behaviour of Nickel and Iron. Circuits in which there is (*a*) no Thomson effect, (*b*) no Peltier effect. Null effect of unequal thickness of wires. Effects of irregular stress and strain in a wire.

CHAPTER XII.

OTHER EFFECTS OF HEAT.

204. In this chapter we propose to collect a few odd remarks on some of the effects of heat, the discussion of which would have unduly interrupted the continuity of the more important divisions of the subject already treated; and to take advantage of the opportunity to introduce others which cannot as yet be strictly classified. We shall thus be able, for instance, to say a few words about some of the chemical aspects of the subject, other than the heat of combination to which the next chapter is devoted.

205. A curious example of mechanical motion, due directly to expansion, is afforded by what is commonly called the *Trevelyan Experiment.* A piece of heated metal is laid on a cold block, usually of lead, so as to touch it at a place which has been recently scraped or filed (to remove the oxide). If the heated mass be of such a form and so placed that it can rock easily on its supports, the rocking (once started) becomes very much more rapid, so much so as to produce a quasi-musical sound which often continues until the two bodies have acquired almost the same temperature. The explanation of this phenomenon, given by Leslie and confirmed by Faraday, depends merely upon the

fact that at the point where the hot metal touches it the cold metal is so suddenly heated that it swells up, thus canting the rocker over to meet with similar treatment on the other side. Before it has come back again to its first position the swelling on the cold block has subsided, the heat having penetrated into the block by conduction, and thus the process is repeated until the temperatures of the two bodies are nearly equal.

The effectiveness of the arrangement is often much increased by filing a notch in the lead, so that the rocker touches the block alternately on opposite sides of the notch.

The rapidity of the vibrations, and therefore the pitch of the note produced, is usually much altered by pressing the rocker more or less forcibly on the cold block ; and, when this process is skilfully conducted, sounds of the most extraordinary character, sometimes almost vocal, are produced.

206. An interesting example of the effect of heat, upon what are usually called "molecular" forces, is supplied by the modifications produced on capillary phenomena.

In general the curvature of the surface of water and other liquids in a capillary tube becomes less as the temperature is raised ; and at the same time the surface tension also becomes less ; so that, on both accounts, the height to which the liquid rises, or the depth to which it is depressed, in a capillary tube, becomes less as the temperature rises.

The former phenomenon is easily seen by careful inspection, and the proof of the latter is established by a multitude of simple experiments.

Thus if a thin layer of water of considerable surface be placed on a large metal plate, and a small lamp flame be applied under the middle of the plate, the effect of the lamp is of exactly the same kind as that which it would produce on a tightly stretched sheet of India-rubber. The surface tension of the colder water overcomes the diminished surface tension of the hotter water, and thus we have the same sort of result as we get by putting a single drop of alcohol or ether on the middle of the water surface. In the course of a little time the water is dragged away on all sides from the heated part, in the one case, as it is in the other case from the point at which the alcohol was applied.

Thus we see why a drop of solder seems to be repelled from the hotter to the colder parts of a soldering iron.

207. Another curious fact, closely connected with this part of the subject, is the effect of the *curvature* of a liquid surface upon the pressure of saturated vapour which is in equilibrium in contact with it.

When a number of narrow tubes, open at each end, dip into water in a receiver (free of air, let us suppose) the water surface is in each raised in proportion as its curvature is greater. Also the vapour pressure is less as the surface is more raised. Hence, the more concave is a water-surface, the less is the pressure of saturated vapour in contact with it. If the tubes be now closed at the bottom, with a little water in each, evaporation or condensation will take place according as the water level is now higher or lower than before, and will proceed until the heights above the external water-surface become the same as when the lower ends were open. W. Thomson, who first called attention to this phenomenon, considers that it accounts for the great amount of water absorbed from damp air by bodies with fine pores or interstices, as cotton-wool, &c. Clerk-Maxwell pointed out that it also accounts for the growth of the larger drops in a cloud at the expense of the smaller ones; and, at least in part, for that collapse of small bubbles of steam, which gives rise to the so-called "singing" of a kettle of water just before boiling commences.

208. This leads us to make a few more remarks on the subject of boiling.

Water boils at a lower temperature in a metallic vessel than in one made of glass.

If water be carefully deprived of air, it is found that with care its temperature may be raised in a smooth vessel many degrees above the boiling point corresponding to the pressure to which the water is subjected. But if some chips or filings of metal, or any solid with sharp angular points or edges, be dropped in, it suddenly boils with violence. It is possible that this property may have something to do with boiler-explosions, at least when no fresh supply of water has been put in for some time before their occurrence.

These facts have not yet been thoroughly explained, but it would appear that a nucleus of some kind is required for boiling, just as (§ 176) it is required for condensation.

209. A very singular example of explosive boiling is furnished by the geysers, or volcanic hot springs, of Iceland. The phenomena exhibited by these were carefully examined by Bunsen and Descloiseaux (Liebig's *Annalen*, 1847).

They determined the temperature of the water at different depths in the shaft of the Great Geyser, at various intervals before and after a grand eruption; and on these observations Bunsen founded his theory of the action which takes place.

Between two eruptions it was found that the temperature of the water in the shaft increased from the surface downwards, but in no place rose so high as to reach the boiling-point corresponding to the sum of the pressures of the atmosphere and of the superincumbent water. The temperature steadily rose at every point, steam and very hot water being supplied from below and probably also at the sides of the shaft until a small upward displacement of the water column into the basin lowered the pressure to the boiling-point at one part of the shaft. This usually occurred at a depth of somewhere about seventy feet under the surface. Then there was violent boiling, blowing out the upper part of the column of water; and thus relieving the lower part from pressure, so that it also boiled explosively. Then colder water, from the geyser basin, ran back into the shaft, and the gradual heating from below recommenced.

It is easy to exhibit the phenomena on a small scale, by artificially producing the observed state of temperatures, and thus to fully verify the sufficiency of Bunsen's theory.

210. In §§ 60, 134, while defining the fixed points of the Newtonian thermometer scale, we used the terms *pure ice* and *pure water*. This implies, of course, that the freezing and boiling points of water (and of other liquids), are affected by impurities held in solution. [Mere mechanical suspension of impurities, as in the case of muddy water, produces in general no measurable effect.]

The most important case, so far as the freezing point is concerned, is when water contains common salt in solution. It is found that the temperature of the freezing point is then notably lowered. Walker (in the *Fox* Expedition) found that the freezing temperature of ordinary sea-water is below 28°·5 F. He observed, however, that a great deal of salt is extruded from the ice. So he melted the ice, and re-froze it, several times in the hope of thus obtaining drinkable water. Although the freezing-point was raised by each operation, the water was still brackish after four repetitions of the process. The lowest specific gravity of the liquid thus obtained was from 1·0025 to 1·002. He also tried the converse process, removing in succession the various ice-crusts formed at lower and lower temperatures from a tub full of sea water, in order to find how strong a brine could thus be procured.

211. Very extensive and careful measurements have been made of the boiling-points of aqueous solutions of various salts, of different degrees of concentration. In all cases the boiling-point is above 100° C., and the amount of rise is approximately proportional to the percentage of salt in solution:—the co-efficient of proportionality being different for different salts. Such solutions, when boiling, give off almost pure water-vapour; and it is sometimes stated that, however high be the boiling-point of the solution, the vapour comes off at the temperature corresponding (in Regnault's table) to the pressure. There can be no doubt, from special experiments made by Regnault and others, that a thermometer placed in the issuing vapour does indicate very nearly this temperature corresponding to the pressure. But it is to be remarked that the aqueous vapour just before it leaves the liquid is certainly superheated; and that superheated vapour leaving the liquid freely in a partially closed vessel soon becomes saturated vapour, which deposits a layer of water on the bulb of the thermometer. The temperature of the bulb is therefore that at which *pure* water is in equilibrium with water-vapour at the pressure to which they are exposed, so that the method of observation is fallacious. We do not yet know, by any certain method, what is the exact temperature of vapour leaving a saline solution, boiling under ordinary pressure at a temperature above 100° C.

212. The rise of the boiling-point produced by salts in solution is attributed to the molecular attraction between the salt and the water. Hence, when the circumstances of

the experiment are altered, so that pure steam at 100° C. is made to pass into an aqueous solution of a salt, condensation of steam (with its accompanying disengagement of latent heat) goes on until the mixture rises to its boiling-point. Thus, with steam at 100° C. such solutions may be raised to temperatures very considerably higher.

In Leslie's mode of freezing water, the greater part of the heat developed in the sulphuric acid is the latent heat of the vapour absorbed. In the next chapter we shall see how to account for the rest.

213. What is called the *spheroidal state* of liquids is a phenomenon which, in one at least of its many forms, has been known from remote times. When a laundress wishes to test whether a flat-iron is sufficiently hot, she dips her finger in water and allows a drop to fall gently on the iron. When the iron is not much above 100° C. in temperature, the drop spreads over the surface, and rapidly boils away. But if it be considerably hotter, the drop glides off from the surface without wetting it, and without suffering much evaporation. [See *Phil. Mag.* 1850, I. 319, and 1832, II. 378.]

The phenomenon is easily studied by dropping water cautiously from a pipette into a shallow platinum dish heated from below by a Bunsen lamp. When the dish is sufficiently hot, the water appears to behave on it very much as it does on a cabbage-leaf or on an oiled or greasy surface. The water is, of course, not in contact with the metal. This can be verified in many ways. For instance, if the dish be slightly convex instead of concave, a ray of light can be made to pass between it and the drop. Poggendorff connected one pole of a battery with the water and the other with the dish, and found that no current passed. The temperature of water in the spheroidal state is found to be about 95° C. only.

The force required to support the drop is easily calculated. Thus, suppose it to be a square inch in lower surface, and a quarter of an inch thick. A water barometer stands at about thirty-three and a half feet at the mean atmospheric pressure. Hence the additional pressure required to support the drop is only about $1/33{\cdot}5 \times 12 \times 4$, or roughly, $1/1600$ of the atmospheric pressure. This is supplied, as will be easily seen when we are dealing with the Kinetic theory of gases, by the momentum acquired by air and vapour particles which have come in contact with the hot surface. On leaving it they move in directions more nearly perpendicular to the surface than those in which they impinged ; *i.e.* more nearly vertical :—and thus, in the very thin layer between the water and the metal, the gaseous medium exerts a somewhat greater pressure in a vertical than in a horizontal direction. To produce a similar result in a thicker layer the gas or vapour must be rarefied, so that the *mean free path* (Chap. XXII.) may be much increased in length.

214. This simple consideration gives the explanation of the chief phenomena shown by the *Radiometer*. This instrument consists essentially of a set of very light vanes attached to an axle, about which they can freely turn. One side of each vane is blackened (so as to absorb heat), the other side is polished. The whole is fixed in a partial vacuum. When it is exposed to radiation there is greater gaseous pressure on the blackened than on the polished sides of the vanes, and the apparatus consequently rotates.[1] The first experimental results which seem to have had a direct bearing on this explanation are due to Fresnel, but they were left unnoticed.

215. With care water may be kept in the spheroidal state in a glass vessel, such as a watch-glass. But to insure success

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[1] Dewar and Tait, *Nature*, xii. 217.

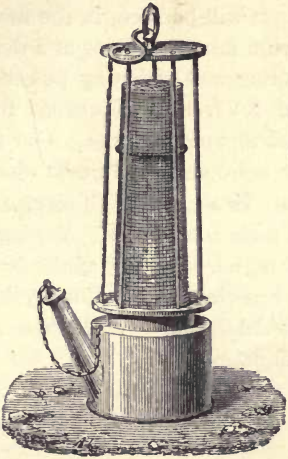
in this experiment the water must be nearly at its boiling-point when it is dropped on the glass. We may even have a spheroid of water above the surface of very hot oil. But here great caution is requisite, as explosions often occur, scattering the hot oil in all directions.

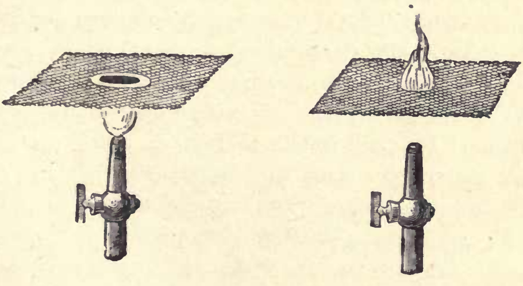
216. Another striking form of the same experiment is to dip under water a solid ball of silver heated almost to its melting-point. The ball is seen to glow in the middle of the water for a few seconds (cooling, however, more rapidly than it would have done in air), when suddenly the water comes in contact with it, a slight explosion occurs, and all is dark. The experiment is considerably facilitated by previously adding some ammonia to the water.

217. Brewster long ago discovered that in many specimens of topaz and other crystals there are cavities, usually microscopic, which are partially filled with liquid. Sang observed that little bubbles of gas in the liquid in the cavities of Iceland spar seem to move *towards* the side of the cavity at which the temperature of the crystal is slightly raised. If part of the walls of the bubble be formed by the solid, the explanation of this curious fact probably involves the capillary phenomena described in § 206 above. But when the bubble is wholly surrounded by liquid, it would seem that the motion is only apparent, the liquid distilling from the warmer side of the bubble and condensing on the colder. As the liquid is usually carbonic acid, and under considerable pressure, this explanation seems to accord with known facts. Very similar phenomena can be produced on a comparatively large scale by holding a warm body near one end of a small free bubble in a horizontal sealed tube containing liquid sulphurous acid.

218. Davy's ingenious *safety-lamp* is merely an ordinary lamp surrounded by wire-gauze. He found by trial that

what is called *flame* cannot, except in extreme cases, pass through such gauze. If we lower a piece of wire-gauze, whose meshes are not too wide, over the flame of a Bunsen lamp, the flame is arrested by the gauze, although the unconsumed gaseous mixture which passes through the meshes is highly inflammable. This may be proved by applying a





lighted match to it. Or we may operate with the lamp unlit, when it will be found that the mixed gases can be inflamed above the gauze without igniting the explosive mixture below it. It will be seen, in the next chapter, that the ignition of such a mixture begins at a definite temperature. The conducting and radiating powers of the gauze (Chaps. XIV. and XVI. below) prevent the heated part from being raised to this temperature. Our further remarks on flame will come more suitably in next chapter.

219. *Résumé* of §§ 204–218. Trevelyan experiment. Effects of heat on molecular forces. Vapour pressure over curved surface of liquid. Boiling under abnormal conditions. Geysers. Freezing and boiling points of aqueous solutions. Spheroidal state. Radiometer. Motion of bubbles. Safety-lamp.

CHAPTER XIII.

COMBINATION AND DISSOCIATION.

220. Refer again to §§ 47, 51, 155—7. As we have already remarked (§ 38), we know almost nothing as to the state in which energy exists in a body. We can measure, in general, the amount which goes in, or which comes out; and we can tell in what forms it does so. But we have seen that molecular changes such as melting, solution, solidification, crystallisation, &c., are usually associated with absorption or evolution of heat. We attribute these thermal phenomena to the work done against, or by, the so-called molecular forces. This is, of course, merely an hypothesis; so framed, however, as to fit in with the law of conservation of energy. The actual nature of the process is wholly unknown to us. It is not to be expected, then, that in the present state of science we should have arrived at anything more satisfactory than this in connection with the profound changes which take place in what is called chemical combination. Still, the little we do know is of great importance from the physical, as well as from the more purely chemical, point of view. And, from the purely practical point of view, it is one of the most important parts of our subject. For it is directly concerned with almost all our artificial processes for producing heat.

221. It might at first sight appear, from some well-known experiments, that no very definite information is to be had on such subjects. For we can make the same two bodies combine in many different ways. Thus, to take a simple example, we may burn a jet of hydrogen in an atmosphere of oxygen, both originally at any one ordinary temperature; or we may mix together, once for all, in the proper proportions, and at the same temperature, our oxygen and hydrogen, and apply a lighted match or an electric spark to the mixture. The one process may be made to take place almost as slowly and as quietly as we please; the other (in a vessel of moderate size) is practically instantaneous,[1] and is accompanied by all the physical concomitants of a violent explosion. But, if we consider the two processes in the light of Carnot's fundamental principle (§ 85), we see that when the water produced in each case is of the same amount, and has reached the same final state, the amounts of energy set free must also be the same. In the case of slow combustion it is given out almost entirely in the form of heat; in the explosion a great part appears at first as sound and ordinary mechanical energy: but both of these ultimately become heat. And the quantity of heat thus produced must be the same in the two cases, when the products have arrived at the same final state. So far, well. But suppose that the mixed gases, just before the explosion, had been raised to a higher temperature than that at which the slow combustion took place, would the whole amount of energy involved in the explosion be the same as in the former case? We simply mention this difficulty for the moment.

222. It would take us far beyond our imposed limits to

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[1] There is a definite rate at which a surface of combination runs along in each explosive mixture of gases, but it is usually considerable in comparison with the dimensions of any ordinary apparatus.

give even a complete sketch, without details, of a subject like this, which has been developed in many directions by careful experimenters. We therefore content ourselves with a mere mention (in addition to what has been said in §§ 69, 155, 156 above) of such facts as the following:—

Heat is developed, often in considerable amount, when gases such as chlorine, hydrochloric or hydriodic acid, &c., are dissolved in water. Part of this heat is, of course, due to the change to the liquid from the gaseous form. But the rest is to be accounted for by the same process as are the facts which follow.

When liquids, *e.g.* sulphuric acid of commerce, alcohol, &c., are diluted with water, there is generally evolution of heat accompanied by diminution of volume.

But it is not always the case that there is evolution of heat in the mere mixture of liquids. Thus, although when 27 parts (by weight) of water and 23 of alcohol are mixed at the same ordinary temperature, the temperature of the mixture *rises* about 8°·3 C.; if we mix 31 parts (by weight) of bisulphide of carbon with 19 of alcohol at the same temperature, the temperature of the mixture is *lowered* by 5°·9 C. Now it has been found by direct experiment that, in the former case, the water-equivalent (§ 183) of the mixture is about $\frac{1}{8}$th greater than the sum of those of the constituents; while in the latter case the excess is only about $\frac{1}{16}$th. On the other hand, the volume of the first mixture is 3·6 per cent. *less* than the sum of the component volumes; with the second mixture it is 1·7 per cent. *greater*. The first of these supplementary facts would tell against the observed results, the second in favour of them. The subject is thus easily seen to be one of considerable complexity, and we cannot farther develop it here.

We may mention, however, that experiments have been carried out with mixtures of the same pair of liquids at various (common) initial temperatures. And it appears probable (according to Berthelot) that the specific heats of mixtures vary as much with temperature as do those of simple liquids—so much so, in fact, that the mixture of bisulphide of carbon and alcohol mentioned above would give rise to *evolution* of heat if both components were originally at a temperature lower than 0° C.

223. The application of the great laws of thermodynamics (§§ 37, 82) to chemical combination is, in its elements at least, a matter of no great difficulty. The experimental part of the work has been carried out with great ability by many investigators, prominent among whom are Andrews, Favre and Silbermann, and (more recently) Berthelot, Deville, Thomsen, and Stohmann. We must confine ourselves to the more salient features of the subject.

It follows from the first law that, if any mixture undergo a definite chemical change without taking in or giving out work, the heat developed or absorbed depends solely upon the initial and final states of the system, and in no way upon the intermediate transformations. This is, in one respect, a great gain; for it much simplifies the reasoning from the results of experiment; but it is also a great loss, inasmuch as it prevents our obtaining (by this means alone) any information as to the nature and order of the successive steps of a complex reaction.

Again, in any transformation which takes place without the application or the giving out of work, the heat developed is the equivalent of the excess of the original over the final potential energy due to the chemical affinities involved. [We have spoken here only of heat *developed.* The reason for this restriction will appear at once from the next statement.]

In accordance with the second law of thermodynamics (or its consequence, the degradation of energy), the final state of every combination is that in which the potential energy of chemical affinity is a minimum; or, what comes practically to the same thing, the reactions which take place are such as to develop the greatest amount of heat. And, conversely, compounds which are formed in this way require for their decomposition a supply of energy from without.

224. Thus, to take a simple case, suppose equal weights of hydrogen to enter into combination with oxygen—no matter how. There are but two compounds which (so far as we know) can be formed, water and peroxide of hydrogen. The heat of combination is found to be nearly 50 per cent. greater for the former product than for the latter. Hence, when hydrogen and oxygen act directly on one another, *water* alone is formed, and the excess of either gas is simply unacted on. And, by the first of the three statements of § 223, if we wished to cause water to be oxidised into peroxide of hydrogen, we should have to *supply* energy equal to the excess of the heat of combination of two atoms of hydrogen with one of oxygen, over that of two atoms of hydrogen with two of oxygen.

Hence we should expect to find, as in fact we do find, that peroxide of hydrogen is essentially an unstable compound. The energy required for the formation of such compounds is usually supplied from some direct reaction (forming a stable compound) which takes place at the same time. Thus peroxide of hydrogen is obtained during the formation of chloride of barium from peroxide of barium and dilute hydrochloric acid.

225. We have seen that a compound, which is formed by the direct action of its components with the evolution of heat, is essentially stable. To decompose it, external energy

is required. Thus, in the case just cited, peroxide of barium and hydrochloric acid are each essentially stable, for heat is given out when either is formed directly from its elements. But a mixture of the two is not stable, for a rearrangement of elements is possible by which farther heat can be developed. Here the energy required for the decompositions is supplied by a chemical process.

But there are many other ways in which it can be supplied. Thus heat itself, as in the formation of quicklime from limestone, may be directly the agent. Light also is effective under certain conditions, as in the decomposition of carbonic acid in the leaves of plants, or of salts of silver on a photographic plate. And the discovery of the alkaline and earthy metals, Davy's grandest contribution to chemistry, was effected by the electric decomposition of their hydrated oxides.

On the other hand, compounds which are formed with absorption of heat are often liable to spontaneous decomposition. This is the case with many highly explosive bodies, such as chloride of nitrogen and the oxides of chlorine.

226. The displacement of one element by another from a compound gives an excellent instance of dissipation of energy. Thus the heat of combination of iodine with hydrogen or other metal is less than that of chlorine with the same metal—and chlorine has, in consequence, the power of decomposing such iodides, setting the iodine free. But the whole of this part of the subject is much more easily studied by measuring the energy, given out during a transformation, in its electrical forms than in the form of heat; and therefore, so far as it is not chemical, it belongs more properly to Electricity than to Heat.

Although all combinations take place in accordance with the laws of energy, these laws alone do not enable us to determine the result in any particular case. We must have special data with reference to each pair of the substances involved. These, of course, can be found only by experiment. As they belong much more directly to Chemistry than to Heat, we cannot enter minutely into what is known of them, but will quote, as a specimen, a few general results of one branch of this extensive subject as given by Berthelot.

Strong acids and *strong bases*, when made to combine in equivalent proportions, each being previously dissolved in a sufficient quantity of water, evolve nearly equal amounts of heat in the formation of stable neutral salts, whatever be the acid or the base.

The heat disengaged is but slightly altered by the presence of greater quantities of water, or of additional quantities either of the same, or of another, base.

Examples of this are furnished by the neutral salts of soda, potash, baryta, &c., with hydrochloric, nitric, sulphuric, &c., acids.

Even in the formation of the alkaline salts of strong acids more heat is disengaged than in the combinations of *feeble* acids with the same alkaline bases.

The feeble acids form, even with the strongest bases, salts which are decomposable by water to an extent increasing with the amount of water, but less as there is greater excess of base or acid present.

The increase of decomposition goes on when water is added, without limit in the case of some feeble acids, but tends to a definite limit with others. But there are instances in which a moderate amount of water wholly effects the decomposition, so that the effect on the thermometer is almost exactly the reverse of that due to the formation of the salt.

227. To illustrate some of the above, and a few further, remarks, we give a little table of roughly approximate values of

HEAT OF COMBINATION.

H^2 with O	68,000	34,000
H^2 with O^2	45,000	22,500
C with O	30,000	2,500
C with O^2	97,000	8,100
CO with O	67,000	2,400

The first column indicates the substances combining, and the proportions in which they combine. Here H, O, C, stand for "atoms" (not "molecules") of hydrogen, oxygen, and carbon, in the chemical sense of the term; so that their relative masses are as 1, 16, and 12. The second column gives the number of units of heat (§ 179) produced when 2 lbs. of hydrogen, 12 lbs. of carbon, or 28 lbs of carbonic oxide, respectively, enter into the oxygen combination indicated. The numbers in the third column give the units of heat set free per lb. of the substance to be oxidised. The processes by which these numbers were obtained were all essentially such as to reduce the compound to the same (ordinary) temperature as that of the components, and to measure the amount of heat given out during the reduction of temperature.

Thus, when a pound of hydrogen is oxidised into 9 lbs. of water, 34,000 units of heat are given out. If it could be directly peroxidised, only 22,500 units would be given out. Hence, to effect the farther oxidation of 9 lbs of water, energy equivalent to the difference of these, or 11,500 units of heat, must be supplied.

And we also see that the number of units of heat set free by oxidising a quantity of carbon at once into carbonic acid, is the sum of those corresponding to the two stages—

formation of carbonic oxide, and its subsequent farther oxidation.

228. Many combinations, even of the most vigorous kind, do not take place at ordinary temperatures. Even the explosive mixture of one volume of oxygen with two of hydrogen requires a start, as it were. If the smallest portion of the mixture be raised to the requisite temperature (as by a match or an electric spark) the heat developed by the combination suffices to raise other portions, in turn, to the proper temperature. It is not yet certainly known how a jet of hydrogen is inflamed by contact (in air) with spongy platinum. It is possible that this may be due to the heat developed by its sudden condensation, in which case this would be a phenomenon of the same class as that just mentioned. But it may be due to the mere approximation of oxygen and hydrogen particles by surface condensation.

229. We are now prepared to consider some of the chief phenomena of ordinary combustion. For the table, meagre as it is, shows how very large are the quantities of heat developed in some of the commonest cases of combination. When the gaseous products of a combination are raised to a sufficiently high temperature to become self-luminous, they form what is called a *flame.* We will take one case with a little detail.

230. An excellent and typical instance, which has been very carefully studied by Deville, is that of a blowpipe flame fed with a mixture of oxygen and carbonic oxide, escaping from an orifice of $\frac{1}{120}$th of a square inch in area under a pressure of from half an inch to an inch of water. The flame proper consists of an exterior cone, three to four inches long, vividly blue in its lower parts and of a very faint yellow at the apex. Within this there is an interior cone, barely half an inch long, which consists of as

yet unignited gas. Just at the apex of this interior cone, where the gases have just *begun* to burn, the flame has the highest temperature, and it is there capable of readily melting even a stoutish platinum wire. The temperature of the flame falls off rapidly from this point upwards. [The velocity of propagation of the combining temperature (footnote to § 221) is obviously that of the jet of gas at the apex of the interior cone.]

To find the composition of the luminous matter at any assigned point of the axis of the flame, Deville employed a thin tube of silver, about $\frac{4}{10}$ths of an inch in diameter, which was kept cool by a current of cold water passing through it. This tube was fixed transversely in the flame, in such a way that a small hole ($\frac{1}{120}$th of a inch in diameter) in its side occupied the assigned position in the axis of the flame, and faced the orifice of the jet. The cold water was made to pass so rapidly as to produce suction through this small hole. Thus a sample of the gases of the flame was carried along in the current of water. This was led, after escaping from the water, through caustic potash to remove the undissolved carbonic acid, and then carefully analysed. In order to determine from what amount of the unignited mixture this combustion product had been furnished, the experimenter had previously added to the mixture a known (small) percentage of nitrogen. This gas, of course, passed almost entirely to the collecting vessel, the only loss being due to slight diffusion through the flame.

A great number of concordant determinations made by this method showed that at the apex of the flame there is practically nothing but carbonic acid (provided, of course, that the original combustibles were mixed in the proper proportion). But, from the apex downwards, the proportion of uncombined to combined gases steadily rose, till at the apex of the interior cone (where the temperature is highest) the uncombined gases formed about $\frac{1}{3}$rd of the whole. This result is, at first sight, somewhat surprising, but its explanation is not far to seek. We must take account of the dissociation (§ 47) due to the high temperature.

231. On the theoretical aspects of dissociation we intend to make some remarks later. Meanwhile we may, roughly, assimilate its laws to those of evaporation. We have seen that a liquid, at any definite temperature, is in kinetic equilibrium at its free surface with its own vapour at a definite pressure (§ 162), so that, at the common boundary, there is constant condensation accompanied by an equal amount of evaporation, with equal continuous disengagement and absorption of latent heat.

Thus, in a compound gas, at least at any one temperature *within certain limits* (which now probably depend on the pressure), there is kinetic equilibrium maintained by a constant amount of dissociation, accompanied by an equal amount of recombination, and also with equal continuous disengagement and absorption of heat, the heat of combination. The percentage of the whole, which is dissociated, rises from zero at the lower limit of temperature (at, and below, which there is no dissociation) faster and faster till about half way, and then slower and slower till the upper limit (at, and above, which the whole is dissociated) is reached. This half-way temperature, at which one half of the gas is dissociated, is called the temperature of dissociation.

When the mixed gases are gradually heated, they cannot *begin* to combine till a certain temperature, depending on the constituents and their relative proportions (in a way not yet ascertained), is reached. Thus we see *how* the explosive mixture (§ 228) requires a "start." And, if the constituents be such as to combine directly with evolution of heat, this commencement of combination is sufficient of itself to raise the temperature, with the effect of producing farther and farther combination. This goes on (provided the gas lose no energy to external bodies) until kinetic equilibrium is established, *i.e.* until the percentage of the mixture which is in the combined state corresponds to the temperature reached by the whole in consequence of the heat of combination set free. If, however, the gas be permitted to lose energy, as by contact with a cold vessel or by expanding and doing work, the process of combination will go on farther and may become complete, in which case the final temperature must be under the lower limit.

Similar consequences may be traced if we suppose that the gases be first individually heated above the higher limit, then mixed, and the temperature gradually reduced.

232. *Résumé* of §§ 220–231. Different modes of combination. Heat or cold produced by mixing. Direct consequences of the Laws of Thermodynamics. Stability of compounds. Displacement. Heat of combination. Combustion. Composition of flame. Dissociation.

CHAPTER XIV.

CONDUCTION OF HEAT.

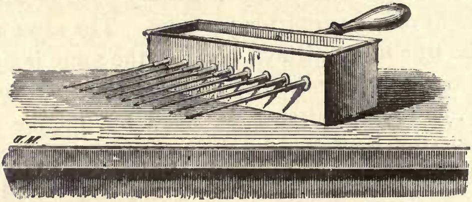
233. REFER to §§ 4, 73. We have already seen that bodies in contact ultimately acquire the same temperature. This experimental fact is the necessary basis of almost all our methods of measuring temperature. The same must, of course, be true of contiguous parts of the same body. This can only occur by transference of heat from part to part of the body. For the present we need not inquire whether this equalisation is effected by the mere passage of heat from the warmer to the colder parts, or whether there is a mutual interchange in which the warmer part gives more to the colder part than it receives from it. So far, indeed, as the ultimate result is concerned, it does not matter which of these is the correct view, for we cannot identify any portion of energy; though the question is theoretically of great interest and importance, as we shall find when we come to *Radiation*. To this latter head also we will refer all cases in which the transfer of heat in a body appears to take place *directly* between parts at a finite distance from one another.

234. That bodies differ very greatly in conducting-power for heat, is matter of common observation. We hold without inconvenience one end of a short piece of

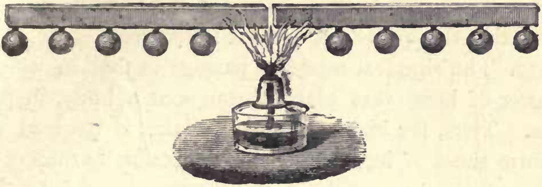
glass, even when the other end is melting in a blowpipe flame. No one would try the same experiment with a similar piece of copper or even of iron. The pieces of wood or bone which are inserted between the handle and the body of a metal tea-pot owe their presence to a recognition of the same fact. So does the packing of the interior of a Norwegian cooking-stove.

Two of the ordinary forms of lecture experiment may also be mentioned here.

First, that of Ingenhouz, in which a metallic trough, from the front of which a number of rods of the same diameter, but of different materials, project. These rods are covered with a thin film of bees-wax, which melts whenever it is raised to the proper temperature. Suppose the whole to be at the temperature of the air, and hot water to be suddenly poured into the trough. By watching the limits of the melted wax we can judge of the relative *thermometric* conducting powers of the various materials.



A less objectionable form of the experiment consists in placing end to end two bars of iron and copper, of equal sectional area, having small bullets attached by bees-wax to their lower sides, and placing a lamp flame impartially between them. The temperature at which the wax softens sufficiently to let the bullets fall is found to travel much faster along the copper than along the iron. And here it *does* really indicate superior conducting power on the part



of the copper, for the thermal capacities (§ 183) of iron and copper are not very different.

235. Some creditable work was done on this subject last century by Lambert. But the first to give a thoroughly satisfactory definition of conducting power, or *conductivity* (*not*, in English at least, conductibility or conducibility) was Fourier. The entire subject of the present chapter, with all but its later experimental developments, may be said to have been created by his *Théorie Analytique de la Chaleur*, first published in a complete form in 1822; and these later developments may be said to have been suggested, or rendered possible, by Fourier's work. Its exquisitely original methods have been the source of inspiration of some of the greatest mathematicians; and the mere application of one of its simplest portions, to the conduction of electricity, has made the name of Ohm famous. And more, in this work of Fourier's, attention was first specially called to the extremely important subject of *Dimensions* of physical quantities in terms of the fundamental units. [See Chapter XIX.]

236. Conducting power must, *ceteris paribus*, be measured by the quantity of heat which passes. We must therefore find how to estimate the amount of heat passing

from part to part of any one body, and what are the circumstances which have influence on it. We can then place two different bodies under precisely the same determining circumstances, and thus compare their conductivities by comparing the quantities of heat transferred.

237. The simplest mode of passage is that in which the transfer of heat takes place, throughout a body, in parallel lines. Thus, for instance, when a lake is covered with a uniform sheet of ice, the ice grows gradually thicker if the temperature of the air be below the freezing point. This is caused by the passage of heat through the ice from the water immediately below it, the upper surface of the ice being kept colder than the lower. Thus the layer of water next the ice freezes. And as the temperature is the same throughout any horizontal layer, whether of water or ice, the transference of heat is wholly perpendicular to such layers, *i.e.* it is vertically upwards.

Hence we choose, as our typical form of conducting solid, a plate of uniform thickness and of (practically) infinite surface, whose sides are kept permanently at two different temperatures. After a lapse of time, theoretically infinite but in general practically short, a permanent state of distribution of temperature is arrived at throughout the slab, and therefore every layer parts with as much heat as it receives. If, under these circumstances, we measure the quantity of heat which passes through a square inch, foot, or yard of any layer of the plate in a minute, we may take this as representing numerically the conducting power. To compare plates of different substances, we must of course take them all of the same thickness, and use the same pair of temperatures for their sides.

Thus we are led to define as follows:—*The thermal conductivity of a body at any temperature is the number of units* *of heat which pass, per unit of time, per unit of surface, through an infinite plate (or layer) of the substance, of unit thickness, when its sides are kept at temperatures respectively half a degree above, and half a degree below, that temperature.*

The units which we employ are, as hitherto, the foot, the minute, the pound, and the degree centigrade. In a special chapter we will show how to pass to any other system of units. [It will be observed that conductivity may, so far as the above definition goes, depend upon the temperature of the body. This will be considered later.]

238. The methods chiefly employed for measuring thermal conductivity depend ultimately upon observations of temperature of the conducting body at different parts of its mass. Thus the amount of heat which passes across any surface in the body, one of the quantities in terms of which the conductivity is defined, is deduced from the change of temperature which it produces *in the body itself.* Now the temperature effects of a given quantity of heat are inversely as the thermal capacity (§ 183) of the body. Hence what we directly deduce from such experiments is not the conductivity itself, as defined above, but its ratio to the thermal capacity. [This ratio is called by Maxwell the *Thermometric Conductivity*, and by Thomson the *Thermal Diffusivity.*] Thus it follows that the determination of conductivity requires that these methods be supplemented by a separate set of experiments for the determination of specific gravity and of specific heat.

239. Let us now think of the state of things in the interior of the slab while a steady passage of heat is going on. The only reason why it goes on is that every layer *differs* in temperature from those adjacent to it. And, because it goes on to the same amount across each (thin) layer, the

difference of temperatures ot the sides of such layer must be proportional to its thickness. [This is easily seen by supposing the layer to be divided into a great number of sublayers of equal thickness, and then considering two, three, or more adjacent ones as a single layer.] Thus the amount of heat passing across any layer depends *ceteris paribus* on the *gradient of temperature* across that layer. This may usefully be substituted for the difference of temperatures of the sides of a layer of unit thickness. For we thus have the means of calculating the amount of heat which passes across any layer, even when there is a variable state of temperature :—as for instance when one side of the slab is kept at a constant temperature while the other is alternately heated and cooled.

240. All experimental results hitherto obtained are consistent with the assumption, which must evidently be true for small gradients, that the amount of heat which passes across any layer, kept at a given temperature, is directly proportional to the gradient of temperature perpendicular to that layer. [It is necessary to point out that the extension to high gradients is an *assumption* found to be consistent with facts, because conductivity is generally measured under circumstances in which the gradient is very much greater than 1° C. per foot, which is that implied in our definition. And we cannot yet positively assert that the quantity of heat which would pass through a slab a millionth of a foot in thickness is exactly a million times as great as that passing through a slab one foot thick, when the surface temperatures are the same, even if the conductivity of the material were the same at all temperatures. The corresponding proposition in electric conduction (which is called Ohm's Law, though directly based on the splendid work of Fourier) involves the same assumption, but here we can much more

easily verify it, and the verification has been carried to extreme lengths by Maxwell and Chrystal.]

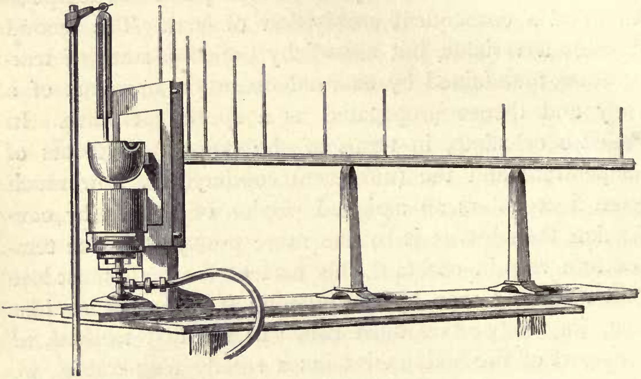
241. It is practically impossible to realise experimentally the simple conditions which are assumed in the above definition of conductivity. Hence, in order to measure the value of this quantity in different substances, experimental arrangements of a somewhat more complex character must be adopted.

Two chief principles have been employed as the bases of experiment. The first requires a steady state of temperature, and a consequent steady flow of heat. The second requires a variable, but essentially periodic, state of temperature, maintained by external causes in one part of a body and thence propagated as a species of wave. In both we calculate, in terms of the (known) gradients of temperature and the (unknown) conductivity, how much more heat enters an assigned portion of a body by conduction than leaves it by the same process. If the temperature remain constant, this part of the body must lose heat otherwise than by conduction; if it do not so lose heat, its temperature must rise. In the first method, as each part of the body maintains a steady temperature, we must measure by some independent process how much heat the assigned portion loses otherwise than by conduction. In the second, we must equate the gain of heat by conduction to the quantity of heat indicated by the thermal capacity of the element and its change of temperature. A third method of some celebrity involves both of these considerations.

242. The first method was employed by Lambert, in an imperfect form: but was afterwards greatly improved by Forbes, who obtained by means of it the first absolute determination of conductivity of any real value. The

principle of the method is extremely simple, but the experimental work and the details of the calculation from it are both very tedious.

A long bar of uniform cross section has one end raised to, and maintained at, a definite high temperature, while the rest is exposed directly to the air of the laboratory. Small holes are bored in the bar at regular intervals; these (when the bar is of any other metal than iron) are lined with thin iron shells, and in them the cylindrical bulbs of accurate thermometers are inserted, each surrounded by a few drops of mercury. [It is found by calculation based on the results of the experiment itself, that these holes do not, to any perceptible extent, interfere with the transference of heat along the bar.]



A second bar, of the same material and of equal cross section, but of much smaller length, also provided with an inserted thermometer, is placed near to the first.

The bars have been left all night, let us say, in the laboratory, no heat being applied. They will then be of the same temperature throughout, viz., that of the air, and all the thermometers will show that temperature. Now suppose heat to be applied to one end of the long bar. [This is usually done by inserting it in a bath of melted solder, or lead, which is maintained by a proper gas-regulator at a steady temperature.] After a short time the thermometer nearest to the source of heat begins to rise, then rises faster and faster. Meanwhile, the next thermometer, in turn, begins to rise. And so on. In Forbes's iron bar, which is 8 feet long by about $1\frac{1}{4}$ inch square section, the final steady state of temperatures was not reached till after a lapse of from six to eight hours. When this steady state was reached (*i.e.* when, for half an hour or more, no change of reading was observed in any of the thermometers) it was found that even the thermometer farthest from the source indicated a temperature perceptibly higher than that of the air of the room, as shown by the thermometer in the short bar. The others showed each a rise of temperature, increasing more and more rapidly as they were placed nearer the source. [The conductivity of copper is so much greater than that of iron, that the farther end of the eight-foot bar has to be kept cool by immersion in a vessel, into which a steady supply of water is admitted from below.] From this experiment, repeated if necessary with different temperatures of the source, it is obvious that we can obtain a very accurate determination of the permanent distribution of temperature along the axis of the bar. [And calculation, by Fourier's methods, shows that the temperature is practically the same *throughout* any cross section of the bar, unless the section be very great, or the conductivity of the material very small.]

243. So far, the investigation has dealt with temperatures only; we must now consider heat. The quantity of heat which passes, per minute, across any transverse section of

the bar, must obviously be the product of the area of the section, the conductivity (§ 237), and the gradient of temperature (§ 239) at that section. The gradient can, of course, be calculated from the observed distribution of temperature, and the area of the section is known. Hence, the heat passing is expressed by a definite multiple of the unknown conductivity. But that heat does not raise the temperature of the part of the bar to which it passes, for we have supposed that the stationary state has been reached. Hence the rest of the bar, beyond the section in question, must lose by cooling in the air (and, in the case of copper, the water-bath at the end) precisely as much as it gains by conduction. It is only necessary, then, to find what amount of heat is thus lost, and we have at once the determination of the conductivity of the bar *at the temperature of the particular cross section considered.* [The words in italics are of special importance, as they indicate one of the most valuable consequences of the improvements due to Forbes, which we now give.]

244. Starting afresh, we *once for all* heat the short bar to a high temperature, insert its thermometer, and leave it to cool in the neighbourhood of the long bar (which is, in this experiment, left at the temperature of the air). The thermometer in the short bar is now read *at exactly equal intervals of time*, say every half minute while it is very hot and cooling fast, then every minute, every five minutes, and finally every half hour, till it has acquired practically the temperature of the air. Some of the thermometers in the long bar are read at intervals during this process. From what we have said above it will be obvious that, from this form of experiment, we can calculate how much heat is lost by the short bar, per minute, per unit of length, at each temperature within the range employed;

and hence we can calculate what was lost in the former experiment at any assigned part of the long bar, since we know what was the stationary distribution of temperature along it.

245. The loss of heat by cooling depends mainly upon the excess of temperature of the bar above that of the air, and it is for the purpose of finding this that we use the two bars in each part of the experiment. But it also depends, to some extent, upon the actual temperature and pressure of the air; and thus the two parts of the experiment should be conducted as nearly as possible at the same air-temperature and pressure. (See § 336.)

246. The unit of heat, in terms of which the conductivity is given by direct comparison of the results of §§ 242, 244, is of course that which raises by 1° C. the temperature of unit volume of the substance of the bar. The results of one of Forbes's experiments on iron, in terms of this unit, are as follows:—

THERMOMETRIC CONDUCTIVITY OF IRON.

Temperature C.	0°	100°	200°
	0·01506 . . .	0·01140 . . .	0·00987

Thus it would at first sight appear that the conductivity of iron for heat, like its electric conductivity, is diminished by rise of temperature. Forbes had expected to find it so, having remarked that the *order* of the metals as conductors of heat is the same as their order as electric conductors, while the electric conductivity of every metal is diminished by rise of temperature. This remark was fully confirmed by the well-planned experiments of Wiedemann and Franz, but Forbes's farther expectation was not, as we shall see, realised.

The following results, in terms of the same or similar units, were obtained by Tait in a repetition and extension of Forbes's experiments. The iron bar employed was that of Forbes.

THERMOMETRIC CONDUCTIVITY.

Temperature C.	0°	100°	200°	300°	
Iron	0·0149	0·0128	0·0114	0·0105	52·9 (1 + 0·0014t)
Copper, electrically good	0·076	0·079	0·082	0·085	53·4 (1 + 0·00088t)
Copper, electrically bad	0·054	0·057	0·060	0·063	52·5 (1 + 0·0009t)
German Silver	0·0088	0·009	0·0092	0·0094	46·6 (1 + 0·0009t)

In this list, all the substances but iron seem to *improve* in thermometric conductivity by rise of temperature.

To convert these numbers into thermal conductivities as defined above (§ 237) they must each be multiplied by the numerical value of the water equivalent of a cubic foot of the corresponding substance, *i.e.* by its thermal capacity (§ 183). These water equivalents are given in the last column of the table. The temperature changes indicated by the factors in brackets are very uncertain.

The following table contains the results of Forbes, with some more recent determinations. Mitchell employed Tait's bars, nickelized to prevent oxidation.

THERMAL CONDUCTIVITY OF IRON AND COPPER.

To foot, minute, and degree C.

Iron.	Copper.	
0·835 (1 − 0·00147t)		Forbes.
0·796 (1 − 0·00287t)	4·11 (1 − 0·00214t) 3·9 (1 − 0·00152t)	Ångström.
0·788 (1 − 0·00002t)	4·03 (1 + 0·0013t) 2·84 (1 + 0·0014t)	Tait.
0·666 (1 − 0·00023t)	2·88 (1 + 0·00004t)	Lorenz.
0·677 (1 − 0·002t)	2·04 (1 + 0·0057t)	Kirchhoff.
0·629 (1 + 0·0007t)	4·14 (1 + 0·0002t) 2·73 (1 + 0·00065t)	Mitchell.

247. It is to be noted, however, that in deducing his final numbers from the data of experiment, Forbes did not allow for the increase of specific heat with rise of

temperature (§ 184). Ångström unfortunately says expressly that this cause can affect the change of conductivity with temperature only to an inconsiderable extent, so that his numbers also are not corrected for this cause. But the specific heat of iron increases by about 1 per cent. for every 7° C., and the introduction of this consideration would reduce to about $\frac{1}{5}$th of their amount the changes of conductivity given by Forbes, and they would then be (in a matter of such delicacy and difficulty) within the limits of experimental error. This change of specific heat has been taken into account by the other experimenters whose results are given above. Thus, it would appear that, though the *order* of the metals as heat conductors is practically the same as their order in electric conductivity, the farther analogy sought by Forbes does not exist. The diminution of electric conductivity by rise of temperature holds for all metals, and nearly to the same extent in all. On the contrary, the thermal conductivity seems (at least in the majority of metals) to improve with rise of temperature.

But it has been shown that copper of good electric quality has higher thermal conductivity than that of bad electric quality. The whole subject, so far as experimental details are concerned, is still in a very crude state, as may be judged from the preceding tables. Of course, a good deal of the discrepancy arises from the fact that the materials operated on differed not only in chemical constitution, but also physically,—*i.e.* having been cast, rolled, drawn, annealed, &c.

248. Ångström's process is the mixed method referred to in § 241. It consists in alternately heating and cooling, for fixed periods and to a fixed amount, one end of a bar, which need not be nearly so long as that employed in Forbes's method. This periodic change is steadily carried

out until the indications of each of the thermometers at different parts of the bar have also become strictly periodic, or at least practically so. Fourier's method, applied to this problem, shows that (at least if the conductivity and specific heat do not vary with temperature) the conductivity can be calculated directly from the rate of diminution of ranges of the successive thermometers, and the postponement of their dates of maximum temperature, per unit of length along the bar; altogether independently of the rate of loss of heat by the surface (provided this loss be everywhere proportional to the excess of temperature over that of the air). The details of the calculation cannot be given here, but a general idea of its nature will be gleaned from the solution of a more restricted problem to be given in the next section, the mathematical part of which may be omitted by any reader without interruption of the continuity of our exposition.

249. Two extremely important practical questions connected with this part of our subject are—

(1.) How does the internal heat of the earth affect (by conduction) the temperature near the surface?

(2.) How far, and according to what law, do the fluctuations of surface temperature, from day to night or from summer to winter, penetrate into the crust of the earth?

The second of these questions obviously involves a problem somewhat similar to that presented by Ångström's method which we have just discussed. And both questions afford us very simple instances of the application of Fourier's beautiful method.

So long as we confine ourselves to the upper strata of the earth's crust, we may treat them as planes, the temperature throughout depending on the depth only, and the passage of heat being therefore in parallel (vertical) lines. This greatly simplifies the investigation.

Let v be the temperature at a depth x under the earth's surface. Then the temperature gradient is dv/dx. Thus the rate at which heat passes upwards through a horizontal area of one square foot, at depth x, is kdv/dx, where k is the conductivity at temperature v. For a depth $x + \delta x$ under the surface this becomes

$$k\frac{dv}{dx} + \frac{d}{dx}\left(k\frac{dv}{dx}\right)\delta x.$$

The excess of the latter over the former denotes the rate at which heat has been (on the whole) communicated to a slab of crust a square foot in surface and of thickness δx.

The rate at which its temperature rises is dv/dt; whence, if c be the thermal capacity (§ 183) of the crust, we have as another expression for the rate at which heat is communicated to the slab, per square foot of surface, and thickness δx,

$$c\frac{dv}{dt}\,\delta x.$$

Equating these independently obtained expressions for the same quantity of heat, we have finally

$$c\frac{dv}{dt} = \frac{d}{dx}\left(k\frac{dv}{dx}\right).$$

This equation is merely the translation into symbols of the final statement of § 241.

250. It is entirely inconsistent with our plan to attempt a full discussion of the varied possible consequences of this equation of Fourier's. We will therefore restrict ourselves to the two particular questions given above. And in each case we will suppose that the conductivity and thermal capacity are constant throughout the range of temperature involved.

251. When there is a steady state of temperature we have

$$\frac{dv}{dt} = 0,$$

whence

$$\frac{d}{dx}\left(k\frac{dv}{dx}\right) = 0, \quad k\frac{dv}{dx} = B, \quad \text{or } v = A + Bx/k.$$

Here A is the surface temperature, and B/k is the rate at which temperature rises per foot as we descend. This might have been obtained at once from the statements of § 239.

Hence *a stationary state of temperature near the earth's surface, maintained by the internal heat, implies a uniform rise of temperature per foot of descent, if the strata are all of the same conducting power.*

If the conducting power be different in different strata, the rise of temperature per foot is greater in each in proportion as the conductivity is less. It is carefully to be observed that, as we are dealing with a steady state of temperature, the thermal capacity of the crust does not appear in our equation.

The quantity of heat which, in one minute, passes through a square foot of area of any stratum, is numerically the product of the conductivity by the rate of increase of temperature per foot of depth.

Very numerous observations connected with this subject have been collected in late years by a committee of the *British Association.* The results vary greatly in different localities, but on the average the rise of temperature in mines, artesian bores, &c., is somewhere about 0°·01 C. per foot. The average value of k may be taken as about 0·024, so that the yearly supply of heat to a square foot of surface from the interior, averages somewhere about 126 units of heat. This is of no consequence in tropical or temperate regions, but towards the poles it forms a minute one among the causes which prevent the formation of an ice-crust of more than some 400 or 500 feet in thickness.

252. Particular stationary periodic solutions of the equation, such as are due to *surface conditions* (any number of which solutions may exist simultaneously because the equation is linear), are necessarily of the form

$$v_0 \epsilon^{-px} \cos\left(\frac{2\pi}{T} t - px + E\right),$$

where T is the period of the disturbance, and $2v_0$ its range at the surface. If we substitute this value in the equation of § 249 we find the condition

$$kp^2 = \frac{\pi c}{T}.$$

Here, of course, we assume k, &c., to be constant; *i.e.* independent alike of temperature and of depth. To introduce temperature changes of these quantities is unnecessary, because the range of temperature in any of these periodic solutions is usually small. And the problem becomes too complex for such a work as this when the strata are supposed to vary (with depth) in conductivity and capacity.

253. Hence, when the earth's surface is subjected for a sufficiently long time to a simple harmonic change of temperature, all layers of the crust have simple harmonic changes of temperature of the same period.

But *the ranges of temperature at successive equal increments of depth diminish in geometrical progression.* The factor for unit of depth is

$$\epsilon^{-p} \text{ or } \epsilon^{-\sqrt{\pi c/kT}}.$$

Thus the range diminishes more slowly with depth if the conductivity be higher, or if the period be longer; more quickly if the thermal capacity of the crust be greater. And, in a precise form, the depth at which the surface disturbance is reduced to a definite fraction of its amount, is directly as the square roots of the conductivity and of the period, and inversely as the square root of the thermal capacity. Thus, as the square root of 365 is about 19, a surface disturbance of a year period will be sensible at nineteen times as great a depth as a disturbance of a day period—provided their original ranges are the same.

Again, *the date at which the maximum temperature arrives at any depth is later in simple proportion as the depth is greater.*

The rate at which the crest of the periodic heat wave travels is

$$\frac{2\pi}{pT} = 2\sqrt{\frac{\pi k}{cT}}.$$

It is therefore directly as the square root of the conductivity, and inversely as the square roots of the period and of the thermal capacity. A rough representation of what takes place in this case may be obtained by imagining waves at sea to run from shallower to deeper water, *i.e.* in the opposite direction to that in which we usually see them coming up a shelving beach, so that their heights shall steadily diminish, instead of increasing, as they progress.

254. Observations of temperature at different depths have been made in various places. The most extensive series is that which, commenced in 1837 by Forbes, has been carried on ever since (with the exception of the years 1876—79, which were occupied in replacing the instruments, which had been destroyed by a madman). These observations are made in the grounds of the Edinburgh Observatory,

where four gigantic thermometers, with their scales above ground, have their bulbs sunk to depths of 3, 6, 12, and 24 French feet respectively, in the porphyritic rock of the Calton Hill. It is found sufficient, so slow are the usual changes, to read these thermometers once a week.

From the sketch, just given, of the theoretical results, we should expect to find the indications of the four thermometers very different in general character:—that nearest the surface being considerably affected by disturbances of short period, which do not penetrate far into the crust; while those of the 24 feet thermometer should depend only upon the surface disturbances of longer periods. This is found to be the case.

255. Fourier has given us a method of decomposing any strictly periodical disturbance, however complicated, into its separate simple harmonic elements. By the aid of this method we can separate from the recorded indications of each thermometer that part which belongs to the yearly change from winter, through summer, to winter again; and to this, as by far the most important, we will confine our attention. We give the approximate average numbers for the years 1837—42.

The mean temperature is about 7°·5 C. at the highest thermometer, and rises steadily to about 8°·1 at the lowest (§ 251). The ranges of the annual wave are, for the various instruments in order—

8°·2, 5°·6, 2°·7, and 0°·7 C.

These do not very accurately follow the law of geometrical progression (§ 253), but from them we obtain, a year being our unit of time, the average value

$$\sqrt{\frac{\pi c}{k}} = 0\cdot115 \text{ per French foot, nearly.}$$

The epochs of maximum temperature are, in order—

August 19, September 8, October 19, January 6.

These follow very closely the arithmetical law (§ 253), and give for the velocity of propagation of the heat-wave

$$2\sqrt{\frac{\pi k}{c}} = 54\cdot8 \text{ in French feet per annum.}$$

Multiplying together the right hand sides, and the left hand sides, of these two equations, we have, as a test of their accordance,

$$2\pi = 6\cdot302\,;$$

which, being within $\frac{1}{3}$rd per cent. of the truth, gives us some confidence in the general accuracy of the work.

Taking, therefore, the quotients of corresponding sides of the equations, we have

$$\frac{k}{c} = \frac{27\cdot4}{0\cdot115} = 238 \text{ nearly.}$$

The value of c for this rock, found directly by Regnault, is about 0·528.

Hence, to the system of units employed, we have

$$k = 125\cdot6.$$

To reduce to British feet we must multiply by 1·136, the square of the ratio of the lengths of the French and the British foot. And, further, to express the conductivity in minutes instead of years, and in terms of the usual unit of heat (§ 56), we must divide by the number of minutes in a year, and multiply by the number of pounds in a cubic foot of water. (See Chap. XIX.) After these reductions we finally find—

Conductivity of Calton Hill porphyry = 0·017,

which may be compared with the numbers in the table of § 246. Forbes observed in the same way the changes of underground temperature at two other stations near Edinburgh, where the materials of the crust are very different. The following are the approximate results:—

Conductivity of Sandy Soil (Experimental Gardens),	0·011.
Conductivity of Sandstone (Craigleith Quarry),	0·043.

It was the average (0·024) of the three numbers just given, which we employed in § 251 to form a rough estimate of the heat passing annually from the interior of the earth. We may calculate from these results, of course only in the roughest way, that the heat lost at present per annum from the interior of the earth is capable of raising the temperature of its whole mass somewhere about one ten-millionth of a degree centigrade.

256. The records of these deeply buried thermometers, virtually purified as they are from the effects of the more trivial surface disturbances, are extremely valuable as indications of the periodic changes in solar activity. A very remarkable and suggestive collation of them with the corresponding observed development of sun-spots, by the Scottish Astronomer Royal, is to be found in vol. xiv. plate 17, of the *Edinburgh Observations.*

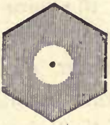
257. Heat conduction is essentially a dissipation of energy: for, whatever be the actual mechanism of the process (see § 233 again), and however short be its duration, there is always necessarily loss of availability incurred by the falling of part at least of the heat from a higher to a lower temperature.

It would lead us far beyond the scope of such a work as this to treat of the Secular cooling of the Earth, or the Age of the Sun's Heat—subjects which have been recently discussed by Sir W. Thomson. Their importance, especially as regards questions of geological time, is so great, that it is to be hoped that before many years have passed, experimental methods may be devised and carried out, capable of giving really satisfactory determinations of the conductivity and thermal capacity of rocks and lavas through wide ranges of temperature. This branch of our subject is especially one in which experiment is as yet far behind theory and mathematical methods.

258. There is, however, one important remark to be made. A *discontinuity* of temperature is impossible in a conducting body, if there be no sudden generation of heat. Hence if, in tracing back by the help of Fourier's methods from a present to the various necessarily precedent distributions of heat, we find that at some definite epoch there was such a discontinuity, *we have a new problem;* we are forced to conclude that this state of matters did not arise by mere conduction, and that there must have existed at that epoch some source of heat not taken account of in our equations. But questions like this are of a higher order of difficulty than those to which an elementary treatise must be confined.

259. Hitherto, the conducting solids we have dealt with have been assumed to be isotropic (§ 100). But special experiments had of course to be made to determine whether bodies which are obviously not isotropic in their molecular structure, such as wood, fibrous or rolled iron, crystals (of any but the first system), &c., are also non-isotropic as regards thermal conductivity. This question was answered in the affirmative: chiefly by the elaborate researches of De Senarmont, who devised the following extremely simple and elegant experimental method.

A thin plate, with parallel faces, is cut from the substance to be examined, the direction of its normal making known angles with the chief axes of structure. The surfaces of this plate are covered with a very thin film of beeswax. A stout wire of copper or silver is passed tightly through a hole bored perpendicularly to the faces of the plate; and is heated to a definite temperature by a lamp (the radiant heat from which is prevented by screens from reaching the plate), or preferably by passing a voltaic current through it. If the plate be of glass, or other isotropic material, the wax melts over a circular portion of the surface (surrounding the hole as centre) which increases more and more slowly till it acquires a definite diameter, which depends on the conductivity, the thermal capacity, and the rate of surface loss, of the plate. But, if the plate be cut from a non-isotropic substance, the boundary of the melted wax is usually an ellipse (the centre still being at the hole). The cuts represent, roughly, the effect when the plate is of quartz cut (1) perpendicular, (2) parallel, to the axis of the hexagonal prism; along which the conductivity is the greatest. If the substance (as in this case) be homogeneous, the thermal capacity is the same at all points, and thus the results of this experiment are conclusive as to the different conductivities in different directions. By measuring the ratio of the axes of this ellipse and observing their directions, in slices cut with various orientations, we can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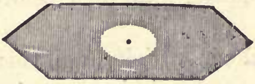
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approximate to the form and position of the ellipsoid at the surface of which a given temperature would be produced in the interior of a mass of the substance by a single point-source of heat.

260. From the mathematical theory of this experiment (which has been admirably given by Stokes in the *Cambridge and Dublin Mathematical Journal*, vol. vi.) it appears that the conductivities parallel to the axes of this ellipsoid (which are the principal axes of thermal conductivity) are proportional to the squares of the lengths of these axes. It also appears from theory that the dimensions only, not the form, of the ellipse on the plate are altered by the surface loss of heat.

When the plate is of moderate thickness, the curves on the two surfaces are usually ovoid rather than elliptical, the smaller ends being turned opposite ways on the two. This arises from the fact that the wire has been passed perpendicularly through the plate. When the hole is bored in the direction of the diameter of the conduction-ellipsoid conjugate to plane sections parallel to the plate, the curves on the two surfaces of the plate are similar, equal, and similarly situated ellipses, with their centres at the ends of the hole.

261. The thermal conductivity in liquids (except mercury and other melted metals) is in general extremely small. We know that the upper layers of water in a vessel may be made to boil, by cautious introduction of steam, while the temperature an inch or two below is not sensibly affected. To the units already employed, the conductivity of water, which is one of the liquids highest on the list, is probably less than 0·01.

The conductivity of gases is still smaller, and therefore very difficult to measure. But it can be *calculated* from the kinetic theory; and we therefore defer its consideration for the present.

262. *Résumé* of §§ 233–261. Mechanism of Conduction. Preliminary illustrations. Fourier's great work. Definition of Thermal Conductivity. Thermometric Conductivity. Gradient of temperature. Fundamental assumption. Experimental method of Forbes. Results of Forbes, Ångström, and others. Ångström's method. Effects of internal heat, and of periodical surface heating, on the earth's crust. Underground Thermometers. Conductivity of crust. Conduction in non-isotropic bodies. In liquids and in gases.

CHAPTER XV.

CONVECTION.

263. Refer to §§ 73, 74. From what has been said above it will be clear that a slight inversion of subjects is now advisable—so that Convection, as being more intimately allied with the matters lately discussed, should take precedence of Radiation, which involves a somewhat different class of ideas.

264. It is a subject of transcendent importance, but also, except in its elements, one of excessive difficulty. And in consequence it has been, and still is—at least in its more practical branches—too much in the hands of mere empirics, and far too little in those of strictly scientific men.

Of its importance, it need only be said that it includes, directly or indirectly, by far the greater part of meteorology, as well as the more humble subject of ventilation. Its difficulties arise principally from the great complexity of almost every one of its problems, not from any doubts as to its fundamental principles, for these (in the main at least) are exceedingly simple. But in applying them, we must know and take account of *all* the circumstances; for in this subject, far more than in almost any other branch of natural philosophy, causes which appear at first sight the most trifling and unimportant often completely alter the very character of the result.

265. As convection takes place entirely by means of the relative motion of the parts of a fluid, it is properly a branch of hydrokinetics, and therefore depends for its full discussion upon principles which we cannot introduce here. But, as all accelerated motion of fluids is due to differences of pressure, we must consider *how* such differences can be produced by heat. A body essentially lighter than its bulk of water tends to rise in that liquid because the excess of vertical pressure on its lower surface, above that on its upper surface, is greater than the weight of the whole body. In the same way, because a portion of air, in the free atmosphere, when its temperature is altered, behaves practically as if it were expanding or contracting *at constant pressure* (§ 127), it will tend to rise if its temperature be raised, and to sink if that be lowered. This is well shown by an ordinary fire-balloon, whose gaseous contents are considerably rarefied by a flame applied at the lower end of the bag, which is open. If it be not inclosed, the rarefied air rises still faster, as may be beautifully shown by gently wafting a cloud of smoke towards a flame burning free in the air. In this case the motion of the smoke indicates exactly the form and rapidity of the currents produced. There is a powerful vertical current, or updraught, over the flame, and a (nearly horizontal) inflow of cold air from all sides towards the flame.

266. The effect is considerably intensified if the lower end of a glass or metal tube, held vertically, be slipped over the flame. This trivial experiment gives the basis of the whole system of ventilation by a shaft or chimney with an

open fire at the bottom. As already stated, the actual calculation of the effect even in this simple way, except to a first rough estimate, is an exceedingly difficult problem:—which, having hitherto defied rigorous treatment, has been solved approximately with the aid of hypotheses suggested by experiment.

In fine summer weather near the sea coast we have constant examples of this process on a large scale, due to the large changes of temperature of the land, while the sea remains nearly constant in temperature during the whole twenty-four hours.

When the land is heated by direct sunshine, it heats the air above it, which rises, and has its place supplied by a horizontal inrush of colder air. This is the *Sea-breeze.* When towards, or after, sunset the land grows cold by uncompensated radiation, the air above it becomes colder than that over the sea. The latter rises in its turn, while the former flows outwards to take its place, and we have the *Land-breeze.*

267. The same thing is well shown by water heated in a flask by a small flame placed below. If a little bran be mixed with the water, we see at a glance the nature of the currents produced. A column of heated water rises steadily up along the axis of the flask, and its place is supplied by colder water flowing downwards near the sides. A constant circulation can thus be maintained if the sides of the flask be kept permanently at a low temperature.

The converse is easily shown if the sides and bottom of the flask be kept at a moderate temperature, and some fragments of ice be put in to float on the water. But, if the sides be not kept warm, and if the ice-supply be kept up, this process fails (as in § 121) so soon as the water attains the temperature of 4°. When things are in this state, the application of hydrostatic pressure restores the circulation, in consequence of the lowering of the maximum density point thus produced (§ 121). Continuing the pressure till the ice is all melted, a distribution of temperature will be arrived at which will prevent currents. These, however, will start afresh if the pressure be relaxed. But the pressure required for this will be of the order of tons-weight on the square inch.

Further experimental data are required for the complete treatment of this subject;—but enough has been said to show that it is one of curious interest, especially as regards the currents in deep fresh-water lakes at a season when the temperature at any particular depth fluctuates about the maximum density point for that depth. These difficulties do not present themselves in the case of sea-water; for, even under atmospheric pressure, it freezes before the temperature falls to the probable maximum density point.

268. We cannot, in a work like this, enter upon the general questions of atmospheric—or of ocean—circulation, though they belong most definitely to our subject. Both problems would be sufficiently formidable even if there were no continents, and if the solid earth were truly spherical. For, not to speak of the earth's rotation, whose influence is noteworthy (as regards, for instance, the production of the trade-winds, and the opposite *sense* of rotation of cyclones in the northern and southern hemispheres), we have to consider not merely the varying amount and direction of the sun's radiation and its consequences on the sea and air, but also the way in which it is occasionally cut off for a time from large regions by the formation of cloud. This one element alone, though of course (§ 9), like every physical phenomenon, absolutely determinate to one who knew all the conditions and could completely

work out their consequences, presents itself to our ignorance in a way which can only be called "capricious";—*i.e.* apparently subject to no law. It is found, however, by trial that, in this as in many other apparently hopeless cases, approximate results may be obtained by using *mean values* deduced from long series of observations. Such results must be sought in works devoted to these special problems.

269. Another illustration of the "capriciousness" of such phenomena will occur to any one who thinks of two strata of liquids of different densities, and which do not mix, in the same vessel. As long as the denser liquid is the lower the equilibrium is stable, and any moderate disturbance (produced, for instance, by raising artificially a portion of the lower liquid into the upper, or by pressing part of the upper into the lower) at once rights itself, the energy applied being dissipated in the form of waves at the surface of separation, spreading gradually from the centre of disturbance.

But when the upper liquid is the denser, the equilibrium is essentially unstable;—so that this arrangement is, of course, not fully realisable in practice. But, in every case in which such an arrangement has been nearly realised, the inevitable up-and-down-rushes have taken place, not over the whole surface of separation, but at two or more places which are perfectly determined though we do not possess the data for predicting them.

At some of these places columns of the denser liquid pour downwards, at the others columns of the lighter liquid ascend. There is, no doubt, an important difference between this case and that of two layers of the same liquid at different temperatures; for, in the latter, conduction (small as it is) very quickly does away with discontinuity at the surface of separation; while in the former, there is usually a capillary surface-tension in the separating film. But the results, so far as the nature of the motion is concerned, are very similar in the two cases.

270. Vertical currents at definite places may thus be at once produced either by heating the requisite part of the lower portions of a fluid mass, or by cooling that of the upper portions. But the effects of cooling part of the lower portions, or heating some of the upper, are usually much less important. Hence the grander phases of *Ocean circulation* (except in so far as they depend on winds, and therefore on *Atmospheric circulation*) are much more dependent upon polar cold than upon tropical heat. On the other hand, those of atmospheric circulation depend more upon tropical heat than on polar cold. For the great temperature effects are produced mainly at the upper surface of the ocean, and at the lower surface of the atmosphere. Hence, if there were no great modifying causes, we should expect to find (on the whole) the lower water, as well as the lower air, coming from both sides towards the equator, and the upper currents of each flowing to the poles.

Similarly, if at any locality in the northern temperate zone there should be a large expanse of heated surface, a column of hot air would rise from it and colder air would flow in from all sides. But, as that coming from the south would have, in consequence of the earth's rotation, a relatively greater eastward motion, and that from the north a relatively less, than the central column, the result would be that the inflow would take place spirally, and the whole would form a vortex (cyclone) rotating in the sense in which the earth turns about the north pole. A down-flow of cold air from above would also give rise to a vortex, but its direction of rotation would be the opposite (anti-cyclone); and, because it takes place from above downwards, it should usually be a less violent phenomenon. These rotations would each be reversed in direction in the Southern Hemisphere. It is to be observed, however, that such results as these would only necessarily follow in the case of an extensive disturbance. Smaller vortices, from waterspouts, dust-pillars, &c., up to some forms of local thunderstorms, in general owe their rotation to fluid friction; and with this we are not now concerned, farther than to say that the *sense* of the rotation produced depends upon merely local circumstances.

271. So far, we have taken no account of aqueous vapour, though the atmosphere usually contains it in considerable amount. It is the effective agent in many of the most important meteorological phenomena;—but we must confine our attention to it only in so far as its efficacy is connected with heat.

Every one knows by experience how thin a layer of cloud or mist suffices to arrest the greater part of the sun's heat. It can only do so by absorbing the heat rays (except in so far as it reflects or scatters them), and thus indirectly heating the air in which it is suspended. Thus the cloud, instead of the earth's surface, becomes the intermediary by which the sun's radiations are given to the air.

But water-substance acts powerfully in quite another way. We have seen how great is the latent heat of steam; we know also that an inch per hour is not an unusual fall of rain; while the greater part of it, at least, comes from the lowest mile of the atmosphere. The "homogeneous atmosphere" is about 5 miles in height: and the water barometer (§ 213) stands at about 34 feet. Hence the mass of lower air, in a column a mile high and a square foot in section, is considerably less than that of 7 cubic feet of water—it is in fact about 360 lbs. only. Its specific heat is (§ 187) about 0·25, so that its thermal capacity is about 90. An inch of rain corresponds to about 5 lbs. of water per square foot, giving out about 3,000 units of heat when condensed from vapour. Hence, if all the vapour were condensed at once, the lower air would be raised in temperature by somewhere about 33° C.! We get a still more striking notion of the magnitude of this result by expressing it in terms of work. It is more than four millions of foot-pounds, or the work of one horse for two hours! In a cubic mile of the lower atmosphere this would correspond to the work of a million horses for fifty hours. [If this number of horses were placed on a square mile they would barely have standing room—each would have just three square yards.] This is, of course, an extreme case, but it shows that there can be no difficulty in explaining, by the mere latent heat of the vapour in the air, the energy displayed in the most violent hurricanes. And this energy came, of course, mainly in a radiant form from the sun. This points directly to the subject of the next chapter.

272. We cannot here discuss how the warm, moist, air cools as it expands on rising, becomes partially warm again by precipitation of water, and so on. Even the convective *equilibrium* of a moist atmosphere is not a very simple question,[1] though almost incomparably easier than that of its motions. Nor can we do more than mention the extraordinary convection currents in the sun's atmosphere; where speeds of one hundred miles per second, and upwards, have been actually measured by perfectly trustworthy methods.

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[1] See a short discussion of it by Sir W. Thomson (*Manchester Memoirs*, 1862).

273. A very beautiful practical application of the principles of this chapter has been made by Joule, who employed it to determine the maximum density point of water, and also to measure the heat-radiation from the moon. The details of his apparatus need not be given, the essential feature being a closed circuit in a vertical plane, filled with fluid. A current sets in when, in consequence of difference of temperature or otherwise, there is a difference of density in the contents of the two vertical parts of this circuit.

274. *Résumé* of §§ 263–273. Mechanism of Convection. Basis of Ventilation. Land and Sea breezes. Causes of Atmospheric and Ocean circulation. Cyclones and Anticyclones. Waterspouts and Dust-pillars. Effects of Aqueous Vapour. Convective Equilibrium. Currents in the Sun's atmosphere. Joule's Convection Apparatus.

CHAPTER XVI.

RADIATION.

275. Refer to §§ 40, 73, 74. The term "Radiant," as applied to Heat, though we cannot hope to get rid of it, is even less defensible than "Specific" or "Latent," whose claims we have already examined (§§ 147, 179). Radiations, like Sounds, are all of one class or family, so that the so-called Radiant Heat is simply *Light.*

The following passage is Query 18 of the Third Book of Newton's *Optics:*—

"If in two large cylindrical vessels of glass inverted, two little thermometers be suspended so as not to touch the vessels, and the air be drawn out of one of these vessels, and these vessels, thus prepared, be carried out of a cold place into a warm one; the thermometer *in vacuo* will grow warm as much, and almost as soon, as the thermometer which is not *in vacuo;* and when the vessel is carried back into the cold place, the thermometer *in vacuo* will grow cold almost as soon as the other thermometer. Is not the heat of the warm room conveyed through the *vacuum* by the vibrations of a much subtiler medium than air, which, after the air was drawn out, remained in the *vacuum?* And is not this medium the same by which light is refracted or reflected, and by whose vibrations light communicates heat to bodies, and is put into fits of easy Reflexion and easy Transmission? And do not the vibrations of this medium, in hot bodies, contribute to the intenseness and duration of their heat? And do not hot bodies communicate their heat to contiguous cold ones, by the vibrations of this medium propagated from them into the cold ones? And is not this medium exceedingly more rare and subtile than the air, and exceedingly more elastick and active? And doth it not readily pervade all bodies? And is it not (by its elastic force) expanded through the heavens?"

276. We know by actual trial that there are sounds which, while painfully affecting certain people, are absolutely inaudible to others whose ordinary hearing is quite as good, and who are as favourably situated with regard to the source of sound. But the cause is not far to seek. Such sounds are always either very grave or very shrill. In other words, there is, for each human ear, a continuous *range* of audible sounds. With the majority of individuals this range is somewhere about eleven octaves, the middle being a note corresponding to about 1,500 vibrations per second. If, therefore, we were to trust to our ears only, we might suppose that periodic compressions and dilatations of air must necessarily be confined to this range, a statement altogether inconsistent with the known dynamical properties of air. But here we have the advantage of knowing (to a great degree of accuracy at least) the nature of the objective phenomenon; and we are thus prepared easily to understand that the limits of our range of hearing may depend to a notable extent upon the mechanism of the organs of hearing. In this sense the range may be regarded as wholly subjective, and we can easily conceive

that animals might exist of greater dimensions than man, whose coarser audition-mechanism would enable them to hear, as continuous sounds, periodic disturbances of air occurring twice or thrice per second. Again, we might conceive of insects whose range of hearing should lie entirely among sounds too shrill to affect any human ear. This is still farther impressed upon us by another well-known result. If a large bell or tuning-fork be struck sharply with a hard body, such as a hammer, the sound produced is at first extremely harsh and unmusical; but, as it gradually dies away, it becomes the pure, proper musical note of the instrument. The metallic clang which is first heard is made up of a great number of notes having no necessary musical relation to one another. But these die out at very different rates, the shriller the faster, so that after a short time nothing is audible but the grave, fundamental note.

But we may go even farther. Very low notes, such as those of the longest pedal-pipes of an organ, are *felt* almost as much as heard; and the same thing is often presented to us in the working of massive machinery, as in factories and engine-shops, where a singularly oppressive and even painful effect is produced on the brain, though we can scarcely call the impression by the name of "sound." It seems, in fact, to be almost devoid of what we commonly call loudness; and sometimes we are only conscious of its having existed, by the exceedingly pleasant feeling of relief which we experience when it stops.

277. Analogy at once leads us to inquire whether there is not something similar in the case of our subjective perception of Light. And the very simplest observations at once suggest that such an idea is at least extremely plausible.

The existence in all civilised languages of terms equivalent to our own red-hot, white-hot, &c., is one of the most striking of these. It shows that men have long been accustomed, as the result of experience, to associate heat with luminosity. When we think of this, in connection with the fundamental fact of observation, that heat always passes from warmer to colder bodies, we are led to look upon the emission of light by a hot body as at least part of this process. When a body is gradually heated in the dark, as for instance a stout iron wire by the passage of a powerful electric current, it first becomes visible by feeble rays of long wavelength, or low refrangibility, only; then, as it becomes hotter, it gives out more of these lower rays, along with others of higher refrangibility. This process continues, if the current be sufficiently powerful, until the wire becomes white-hot, *i.e.* until it gives off all kinds of visible light in something like the same relative proportions as those in which they come to us from the sun. If the current be now interrupted, the wire presents exactly the same continuous series of appearances in the reverse order. But, even when it has ceased to be visible, we *feel* (on holding the hand *below* it, so as to avoid convection currents) that it is still giving off something, but at gradually-diminishing rate, which produces the sensation of heat. Bearing in mind the analogy of sounds, and also the fact that the shriller sounds correspond, like the more refrangible rays, to the shorter periods or the shorter waves, we are led to the conclusion that radiation is all one continuous phenomenon, of which only a certain range affects the eye, while below that range it can be detected directly only by the far inferior sense of touch.

278. This, however, is presumption only:—though on very strong grounds. To make the matter certain we must investigate the behaviour of the invisible radiations, and

compare it under conditions as varied as possible with that of the visible. Thanks to the thermo-electric pile, and the galvanometer (§§ 50, 62), we can now treat obscure radiations with an amount of accuracy which, though far inferior in many respects to that usually attainable in optical processes, is sufficient for our purpose.

[Some of the fundamental facts in Optics must here be assumed. We cannot digress to indicate the nature of the evidence for their truth.]

279. In free space, or in air of uniform density, light moves in straight lines. So does radiant heat, whether from the sun or from a terrestrial source. For an opaque obstacle which intercepts the light intercepts the heat also, whatever be the source.

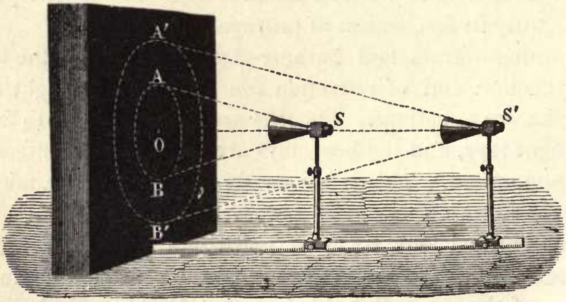
Radiant heat is propagated with a speed practically the same as that of light. After a total eclipse of the sun, the heat rays reappear (as nearly as can be tested) simultaneously with those of light. They are therefore propagated with a speed of somewhere about 186,000 miles per second. This great common speed alone is almost sufficient proof of identity in mechanism of propagation.

Burning-mirrors and burning-glasses show that the laws of reflection and of refraction are the same for light and for obscure radiations. For they are adjusted so as to focus the light rays, and the heat rays are also found focussed at the same place. This is rigorously the case with a mirror, but not so with a lens. To obtain the most powerful effect with a burning lens, we must place it a little farther from the screen than if we wished to obtain the sharpest luminous image of the sun. But the fact that it is so affords a still stronger argument in favour of our proposition, for the focal distance for red rays is greater than that for blue rays (unless the lens be achromatic for these two sets of rays), and we should expect the focal distance to be still greater for lower radiations.

Experiments with a burning-glass are, of course, of a very rude character; but Lord Rosse, and others, have found that, to throw the obscure rays from a star upon a small thermo-electric pile, by means of the mirror or the object-glass of the largest telescope, it is only necessary that the luminous image should be formed on the pile.

280. The intensity of light proceeding from a small source through a transparent medium is inversely as the square of the distance from the source. The thermo-electric pile shows us that the same is true of radiant heat. But this is no additional analogy, for it is necessarily true of any form of energy which spreads *rectilinearly* in all directions from a small source; always provided that none is absorbed by the way.

A luminous surface appears of the same brightness whatever be its distance from the eye (provided there be no absorption of light by the intervening medium). Similarly,



when the conical collecting mirror of the thermo-electric pile is turned towards a uniformly hot surface, the effect on the galvanometer is the same at all distances, so long at least as the surface appears from the pile to fill the entire aperture of the cone. This, again, is a mere consequence of rectilinear propagation, without absorption by the way.

A uniformly luminous surface appears equally bright all over, however various may be its inclinations at various points to the line of sight. Similarly, when a large hot surface of uniform texture radiates to the pile through an aperture, the amount of heat received is not altered by altering the orientation of the surface, so long as (seen from the pile) it appears completely to fill the aperture. Hence it follows that the intensity of radiation, whether luminous or obscure, from a hot surface, in any direction, is proportioned to the cosine of the angle which that direction makes with the perpendicular to the surface. [We shall find presently that this is a necessary consequence of the fundamental tendency of heat to uniformity of temperature.]

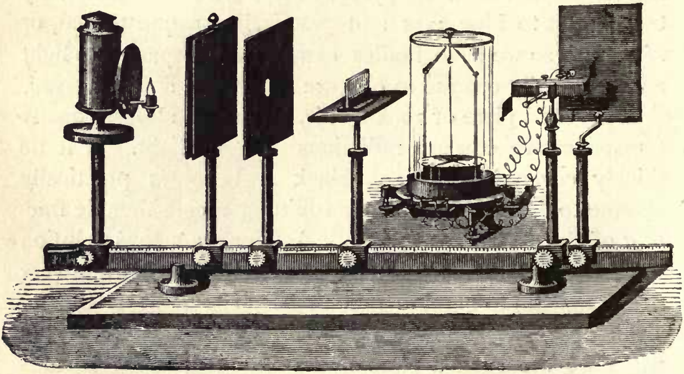
281. Bodies differ extremely from one another in the amount of light which they absorb. The same is true as regards radiant heat. But, just as there are bodies extremely transparent to blue rays and practically opaque to red, or *vice versâ*, so we have bodies extremely transparent to light and practically opaque to obscure radiations, and *vice versâ*.

A polished plate of rock salt is, when dry, almost equally transparent to obscure radiations and to light. If it be thickly covered with lamp-black it becomes practically opaque to light, while still transmitting a considerable fraction of the obscure radiations. A strong aqueous solution of alum is almost perfectly transparent to light, while very nearly opaque to obscure radiations. The same is true of a thick plate of glass:—as is nowadays practically recognised when we use such a plate as a fire-screen, which permits us to enjoy the cheerful light of the fire without suffering unduly from its heat.

282. But there is a farther analogy connected with this. Light, which has passed through one plate of coloured glass, and has thereby been weakened, is much less weakened by passing through a second plate of the same glass, still less by a third, and so on.

So if, by using a sufficiently powerful radiating source, we force a considerable quantity of obscure radiations to pass through a sheet of ordinary plate-glass, the ray so sifted is capable of passing in much greater per-centage through a second plate, and so on.

283. All the facts above described (§§ 279-282) can now be established without the least trouble by the use of the pile and galvanometer. There is no need of describing the obvious necessary adjustments. All this part of our subject was excellently worked out by Melloni, who extended in various directions the valuable work of Leslie. A sketch of the arrangement of Melloni's apparatus is subjoined. It requires no explanation.



284. We might mention a great many more of these less perfect analogies, but the above must suffice. We now

come to others which are practically conclusive of the identity of mechanism in all kinds of radiation. They are, in fact, simply those which established the *Undulatory Theory of Light.* When they were found true of radiant heat also, the identity of the phenomena could no longer be doubted. For this part of the subject we are again indebted to Melloni, and also, in a special manner, to Forbes. It is curious to notice that the original speculations of Mohr, of date 1837, as to the true nature of heat were mainly based upon these discoveries. We will content ourselves with a very brief statement, because the experiments are far more striking when their results are directly exhibited to the eye by luminous rays, than when these have to be groped for, as it were, in darkness by the help of the thermo-electric pile.

285. Every one knows that the establishment of the undulatory theory of light was aided to a wonderful degree by Young, mainly by his doctrine of *Interference* and its consequences. Exact measurements of these phenomena gave the means of determining the *wave-length* of any particular ray; and a very simple adjustment gave the means of proving that light moves faster in air than in glass or in water, and must therefore be due to a transference of energy and not to a transference of material particles. But all this gave no information as to the *nature* of the wave-motion. It proved merely that, along the path of a ray, some kind of displacement occurs which is *exactly* and periodically reversed every half wave-length This might be of the nature of compression and dilatation merely, as in a sound wave; it might be wholly transverse, as in a pianoforte wire; or it might be partly longitudinal and partly transverse, as in ripples or waves at the surface of water.

But the phenomena of *Polarization* at once gave further information. They showed that the displacement, whatever be its nature, must be transverse to the ray; and they enabled Fresnel to give a consistent theory of Double Refraction, and of Circular and Elliptical Polarization.

All the details of these splendid investigations properly belong to *Optics*. We confine ourselves to the mere mention of the simplest proofs of Interference and of Polarization in the case of obscure rays, for these are the keys of the position.

286. Fizeau and Foucault found that all the ordinary interference experiments, such as that with Fresnel's inclined mirrors and that of ordinary diffraction, succeed with obscure rays; and, as was to be expected, indicate greater wave-lengths than those of visible light.

Forbes was the first to obtain positive proof of the polarization of obscure radiations. The form of apparatus which he employed is still amongst the best for that purpose. It consists merely of a stout plate of mica, split by cautious heating into a great number of exceedingly thin parallel films. This is placed inside a tube, at the proper inclination to the axis, and polarizes by transmission just as a parallel bundle of "microscope glass" polarizes light. When two such tubes are placed end to end, between a non-luminous source of heat and the end of the pile, it is found that, if the mica plates in the two are parallel, a considerable amount of obscure radiation is transmitted. This is greatly reduced by making one of the tubes rotate through a right angle; and is restored to its original value by a farther rotation of one right angle. Similar results though not quite so well marked, are obtained with sources hot enough to be self-luminous. But the mica bundles require to be placed at a special angle for each class of radiations so as to give the greatest effect.

We may merely add that the electro-magnetic rotation of the plane of polarization of light, discovered by Faraday, has been found to hold good for obscure rays also.

In comparatively recent years it has been conclusively shown by Clerk-Maxwell, mainly by theoretical deductions from Faraday's wonderful series of experiments, that Radiation generally is an electromagnetic phenomenon. But to discuss his theory, or even to describe the ingenious experiments by which Hertz and others have recently illustrated it, would involve a digression of a much more extensive character than any which have been admitted into this very discursive volume.

287. *Résumé* of §§ 275-286. Radiant Heat is merely Light. Analogy from Sound. Comparison of visible and invisible Radiations, as to speed of propagation, reflection, refraction, absorption, &c. Proofs of identity furnished by Interference and by Polarization. Clerk-Maxwell's Electromagnetic Theory.

CHAPTER XVII.

RADIATION AND ABSORPTION.

288. THE remarks in the preceding chapter, coupled with a mere reference to the radiations of shorter wave-length than those of light (which are studied either by means of fluorescent bodies, or by their action on photographic plates), entitle us to speak of radiation as one phenomenon. Different modes of experimenting are specially adapted for special properties of rays of different wave-lengths, that is all. But the indications furnished by the pile, being independent of particular nerves, or particular chemical compounds (on which sight and photographic processes depend), are obviously fitted, in a special manner, to give us information of one standard kind for all species of radiation alike.

289. If we think again of the phenomena presented by a hot wire (§ 277), we see that we may now state that such a body gives off radiations of all wave-lengths, from the longest up to a certain limit, which depends upon its temperature. The higher the temperature, the higher is the limit, and also the greater is the amount radiated corresponding to each wave-length longer than the limiting one.

290. This prepares us to see that the radiation from a body depends upon *itself* alone (*i.e.* upon its constitution, its

temperature, the nature of its surface, &c.), and therefore that the equilibrium of temperature which ultimately obtains among bodies within an inclosure which contains no source of heat (§ 4), is arrived at, not by the warmer bodies alone radiating to the colder, but by all the bodies simultaneously radiating, each to an amount depending on its own nature, surface-condition, and temperature. Also that equilibrium, once attained, is maintained by the same process. This is called the *Theory of Exchanges*, and was propounded by Prevost last century. He was led to it in trying to explain what had been called radiation of *Cold;* as when, for instance, a thermometer in a warm room falls if a piece of ice be held in the neighbourhood of its bulb.

In 1858 and 1859, respectively, Stewart and Kirchhoff greatly extended our knowledge of this subject, both by experiment and by theory. Their chief theoretical result, however, had been to a great extent anticipated by Stokes about 1850, by the help of a dynamical analogy.

[In the immediate farther discussion of this subject we will suppose that our experiments are all carried out *in vacuo.* This practically restricts our reasoning to solids, which is of course a great limitation; but, *per contra*, it frees us from all the complications of convection. In another chapter we will consider the effects of simultaneous radiation and convection.]

291. It was well known to Leslie and others that the amount of radiation from different bodies, at the same temperature, varies greatly with the nature of the radiating surface. Leslie, for instance, constructed a large cube of tinned iron, one vertical face of which was left bright, a second dimmed by scratching with emery, the third covered with lamp-black, and the fourth with white enamel. When the cube was filled with hot water, it was found that there

was very little radiation from the polished surface, considerably more from the scratched one, but *very* much more from either of the others, which (in spite of their contrast of colour) behaved nearly alike. The amounts of radiation from the polished and the black surfaces are so different that this observation can be made by the sense of touch merely—by holding the hand parallel to these sides in succession, at a distance of a few inches.

292. Leslie, and afterwards more fully De la Provostaye and Desains, made numerous experimental determinations of the radiating, absorbing, and reflecting powers of bodies for the groups of obscure rays from each of many different sources. These experiments cannot lay claim to great exactness; but they tend to show that, on the whole, the radiating and absorbing powers of one and the same body are proportioned to one another, while the reflecting power diminishes as the other two properties simultaneously increase. The apparently anomalous behaviour of some bodies, especially as regards their comparative reflective powers for obscure and for luminous radiations, prevented any grand generalisation from these experiments.

The whole subject, as we now know, is so intimately connected with Carnot's *Principle of Reversibility* (§ 83) that every experimental development which it has received must be looked at from this great theoretical point of view. And this principle, whether an author was aware of it or not, has been the basis of all sound theoretical reasoning on the subject. But, just as Carnot's principle itself is (as will be shown later) exact only in a statistical sense, due to the extreme minuteness of the particles of matter in comparison with our instruments for measuring temperature; so any conclusions we may deduce from it are subject to the same limitations. It is therefore vain, at least in the present state of science, to look for a truly *rigorous* investigation of the relation between radiating, absorbing, and reflecting powers. In all the professedly rigorous investigations which have been given, the careful reader will detect one or more steps which are to be justified only by the statistical process of averages. Why not, therefore, boldly begin by assuming its validity, and thus acknowledging that the demonstration is not rigorous? To avoid unnecessary complication, without in any way losing accuracy, we adopt a method which has been found of great value in older branches of physics.

293. When, in elementary dynamics, we consider the equilibrium of a lever under various forces, we simplify the mathematical treatment of the question in a very marked degree by assuming the lever to be rigid. And we find that we thus obtain a solution of a practically accurate character. If the lever be very long, or the forces very great, such a solution is not sufficient, for we find by trial that flexure takes place. But, unless the flexure be great, we can determine its amount and consequences by means of a simple hypothesis as to the law of bending, and this in turn enables us to obtain in the more complex problem results accurate enough for all practical purposes. Hooke's Law, Coulomb's Laws of Friction, &c., are all mere approximations to the truth, based on experiment, and employed to enable us to avoid difficulties of theory as well as labour of calculation. So with the assumptions of perfect fluids, and of gases which exactly follow Boyle's Law. No such thing as a rigid body, or a perfect fluid, has yet been met with: but the conception of either presents no difficulty, while it affords valuable facilities for simplifying our investigations. And a similar set of assumptions will greatly help our present work.

294. (1.) Though no substance is *perfectly transparent*—all the most transparent bodies being found to be more or less coloured when taken in sufficient thickness, and thus to absorb some of the light which falls upon them, while they also reflect or scatter a portion of it:—we can imagine, and use for reasoning, a perfectly transparent non-reflecting body. Every ray, whether luminous or obscure, which falls on such a body, passes through it without loss.

(2.) A well-polished surface of metallic silver suggests by its behaviour the theoretical conception of a *perfectly reflecting* surface. No ray can penetrate into a body provided with such a surface.

(3.) Similarly, a lump of gas-coke, or a body covered with lamp-black, suggests the conception of a *perfectly black* body. Every ray which falls on such a body is at once absorbed. Hence such bodies can neither reflect nor transmit.

Bodies belonging to one and the same of these three classes have properties (so far as we are concerned with them) absolutely identical.

(4.) A thick plate of cobalt-blue glass, which transmits only one class of rays (red), suggests the conception of a body *partially transparent for one definite ray and perfectly absorbent of all others.*

(5.) Certain compounds of didymium, &c., suggest a body *partially absorbent of one definite ray and transparent to all others.*

(6.) And, finally, a thin film of metallic silver, such as is now used for the glass mirrors of reflecting telescopes, suggests an ideal body *partially transparent to a certain definite ray and a perfect reflector of all others.*

Bodies belonging to any one of these three classes may have properties entirely different from one another.

Various other combinations easily suggest themselves, but those named above are the most important for our object.

295. Recurring to our fundamental experimental fact, viz. that all bodies in an impervious inclosure, which contains no source of heat, ultimately acquire and maintain the same temperature (§ 4), we see that the state of each is altogether independent of the others. Any number of them may be removed, or any number of new ones introduced, without disturbing the equilibrium, always provided they be at the common temperature. [It might be thought that a perfectly reflecting body would form an exception. But if it, and its contents, were originally at the assigned temperature, they would remain so indefinitely. In fact its surface becomes part of the boundary of the original inclosure, while it is also the boundary of an inclosure within an inclosure.] Hence the total radiation, either way, passing perpendicularly across an elementary unit of surface inside the inclosure, must be the same, to the quality and quantity of each of its components, for all positions and for all orientations of the element. For it must remain the same whatever additional bodies at the same temperature are inserted. As one of these bodies may be a black body, the total radiation as above defined must obviously be that of a black body at the particular temperature. This is the aggregate of an infinite number of components, each belonging to a definite wave-length.

This statement virtually contains the whole theory. To make its consequences more clear, we must now fix our attention on one of the components only. In front of a black body in the inclosure, this is supplied entirely by emission, because such a body can neither reflect nor transmit. But if we now suppose a plate of the substance (5) of § 294, at the proper temperature, to be interposed between our place of observation and the black body, the radiation of each particular wave-length will remain unchanged, even of that to which alone the plate is impervious. Hence what the plate absorbs on one side it must, under the circumstances supposed, radiate on the other, exact both as to quality and quantity.

The student may exercise himself profitably in obtaining the same result by supposing the plate to be of either of the ideal kinds (4) or (6) of § 294. And he may then make use of other suppositions of a less restricted character. From all, however, he will find the same common result. We must have proper terms in which to express it.

Let us then *define* as follows :—

The *Emissivity* of a body, for a particular wave-length, is the ratio of that part of its radiation to the corresponding part of the radiation of a black body at the same temperature.

The *Absorptive Power*, for a particular wave-length, is the fraction expressing the portion of incident radiation of that wave-length which is absorbed at a given temperature, the rest being reflected, scattered, or transmitted. [Strictly, the radiation here referred to is that from a black body at the same temperature as the absorbing body; but we *assume*, with probability, that these restrictions are unnecessary.]

With these definitions we see that for all bodies :

The emissivity, and the absorptive power, at any one temperature, and for any definite wave-length, are equal to one another.

296. This is the general proposition, undoubtedly true, as already stated, in a statistical sense. The proof which we have given, or indicated, above was (in all essential particulars) communicated by Stewart to the *Royal Society of Edinburgh* in March 1858. His process, so far as theory is concerned, is apparently much more elaborate than that

just given, and was applied chiefly to obscure radiations.[1] Still more elaborate is that given by Kirchhoff in 1859, and since developed by others with the help of an imposing array of symbols. But all these methods really involve no more than we have given above, and the unnecessary complication, which adds nothing to the soundness of the proofs, tends to prevent the reader from appreciating the comparatively simple, though not rigorous, foundations on which all of them are ultimately built.

297. The dynamical analogy, given by Stokes about 1850, was called forth (like the investigations of Kirchhoff) by the phenomena which gave the first hint of the modern process of *Spectrum Analysis.* Here we must make a slight digression.

Fraunhofer observed in 1817 that the flame of a candle, when examined by what we now call a spectroscopic process, showed a double *bright* line in the orange region exactly where the solar spectrum showed the double *dark* line which he called D. Hallowes Miller, with improved optical means, found the coincidence absolute. But Foucault, in 1849, went farther. Finding this double bright line in the electric arc, he examined the spectrum of sunlight which had passed through the arc, and to his surprise observed that the double dark line appeared darker than before. He then, by means of a mirror, reflected through the arc the light from one of the incandescent carbon points. This light (from a nearly black body) gives of itself a continuous spectrum, parts of which are somewhat brighter than others. But when it was analysed, after passing through the arc, it was found to have dark lines exactly where the arc itself gave bright ones.

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[1] See his own statement in *Phil. Mag.* 1863, i. 354.

298. Stokes explained the phenomena by an analogy drawn from sound. Suppose a space to contain a very large number of tuning-forks or pianoforte wires all tuned to the same note. If they were set in vibration, that particular note alone would be given out. But if a listener were placed at one side of the space, while a cornopean was played at the other, the listener would hear (except so far as mere obstruction is concerned) any note played, *except the particular note to which the strings are tuned.* The strings, in fact, would all be set in vibration by that note, whose energy would thus be greatly diminished. Thus the strings form a medium which, when agitated, gives one definite sound; and which is, at the same time, specially opaque to that particular sound when it originates from an external source.

This is precisely the equivalence of radiating and absorbing power for one definite wave-length. And it may be the very sort of mechanism on which all radiation depends.

299. Now all flames, especially in places near the sea, contain small quantities of common salt, and Swan had definitely proved that the double bright line observed by Fraunhofer in a candle-flame is due to the presence of this substance. Hence it followed from Stokes's reasoning that the production of the double dark line D in the solar spectrum must be due to salt, or rather to metallic sodium in a vaporous form, somewhere between the body of the sun and the earth.

This part of the subject, so far as light is concerned, was very ably worked out by Kirchhoff; but the more close consideration of it belongs to treatises on *Light*, and specially to those on *Spectrum Analysis.*

300. There is, however, one part of the question to which, though it may easily be deduced from Stokes's

dynamical analogy, Stewart and Kirchhoff first called attention. That there may be a *reversal* as it is called, *i.e.* a dark line in a spectrum instead of a bright one, the absorbing medium must be at a temperature so much lower than the source that a black body, at that temperature, radiates *less* of the particular ray than does the source. This follows at once from the main proposition (§ 295), coupled with the fact that the emission of a black body, for any one wave-length, increases as the temperature is raised (§ 277). This also can be derived from the general theory of § 295 by supposing two bodies only to be in our inclosure, both of the *same* material, of the species (5) of § 294, but originally at different temperatures.

Kirchhoff's investigation was direct, and specially limited to single, definite wave-lengths. And it was experimentally verified by the fact that when the source was an incandescent lime-ball, and the absorbing medium the flame of a Bunsen lamp, no reversal of the sodium line took place; while, when a spirit-flame was substituted for the Bunsen, it was obtained at once.

Stewart also operated with light, but did not confine himself (as he might easily have done) to one particular wave-length. He showed that red glass, for instance, loses all colour in the fire when it is at the same temperature as the coal behind it, appears *red* when a hotter coal is behind it, and *green* (the complementary colour) when the coal behind it is not so hot as it is.

301. When giving the general demonstration in § 295, we did not allude to polarization as one of the characteristics of a ray. This we purposely left to a subsequent section, to avoid confusion to the reader. But, if we now revert to the demonstration above, we easily see that a few additional words will meet this consideration also. For, among the

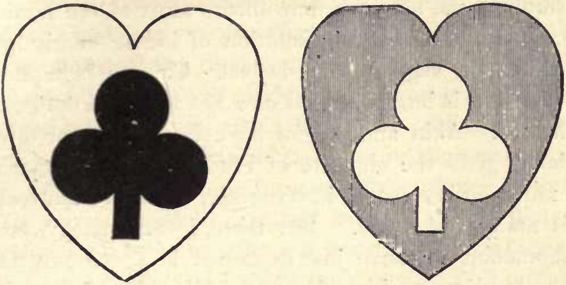
bodies in the inclosure, some may polarise by reflection, some by transmission, as we know they do with light-rays. But the radiation *must be throughout* of the identical character of that from a black body, and thus cannot be polarized. (If this were not so, the mere turning of the black body into a new position would alter the character of the radiation in the inclosure.) Hence a body which polarizes the reflected radiation in one plane, must give off by emission in the same direction light polarized in a plane perpendicular to the first. And similarly with a tourmaline plate which polarizes by transmission. It does so because it absorbs one of the polarized rays produced by its double refraction; and, absorbing, it must also radiate, that definite polarized ray.

This very beautiful and important instance of the truth of the general theory was given, independently, by Kirchhoff and by Stewart.

302. Other instances, but not so simply or directly connected with the theory, may be given in great numbers. We take only a few common ones, easily tested.

If we write with ink on a piece of polished platinum foil, and heat the foil in a non-luminous flame, such as that of a large coal-gas blowpipe, it becomes covered with a thin dark coating of oxide of iron where the ink was applied. When the whole is very hot, the writing appears bright on a dark ground. It does so by radiating more than does the polished surface. But, because it radiates more, that part of the foil is permanently colder, as is seen when the writing is turned to the flame, for the back of the foil now shows dark letters on a light ground.

If pieces of china-ware or crockery, with a dark pattern on a light ground, are strongly heated in a bright fire, we find, on examining them in a dark room, the pattern *reversed.* It is very instructive to flash a ray of sunlight on them at intervals, and then withdraw it, while they are still very hot. The reversed and direct patterns are thus seen alternately in rapid succession.



When we heat a piece of gas-coke to a high temperature it becomes brilliantly luminous. But rock-salt melted, and at the same temperature, is scarcely visible in the dark. The one is very nearly a black body, the other almost a transparent one.

When an incandescent body, in an inclosure, is separated from a colder body by a screen, the ultimate result (unless the screen is a perfectly reflecting body, in which case there are two separate inclosures) must of course be equalisation of temperature, whatever be the particular classes of rays absorbed by the screen. Hence if the screen be very transparent for the obscure rays (which have by far the greater share of the whole energy emitted) while practically opaque to the luminous rays, the colder body may be raised to incandescence before the screen gives off any visible rays. Thus a burning lens of rock-salt is but slightly heated by direct sunlight even when its surfaces are smoked: and, therefore, if of sufficient aperture, performs its proper function of raising bodies to incandescence at the focus, though it is practically opaque to visible rays. Instead of smoking the lens, we may absorb most of the luminous rays by means of a strong solution of iodine in bisulphide of carbon, as suggested by Debus. Caution is required if this solution is interposed *between* the lens and the body to be heated. Akin and others have imagined that this experiment gives the opposite of Fluorescence—*i.e.* that here the radiation is elevated in character, while in Fluorescence it is always degraded. But there is no analogy, for the phenomenon we have just described is a consequence of the general proposition (§ 295), while Fluorescence is, as we shall see, at least apparently an exception to that theory. Of course it is to be remarked that the theory does not *exactly* apply to this phenomenon, for it is essentially connected with a state in which thermal equilibrium is not yet attained; while the theory is based entirely upon the assumption of thermal equilibrium.

303. In all that precedes, we have for simplicity assumed that emission is a mere surface-operation, like reflection or scattering. For these last never take place in the interior of a body except where there is heterogeneity, and in that case the interface between different portions may be looked upon as a new surface. And (except in a passing hint in the preceding section) we have entirely omitted all reference to *fluorescence.*

But the first inspection of a wedge of coloured glass (when the colour is not applied as a mere surface layer) suffices to show that absorption is not confined to the mere surface; and we should consequently expect to find that emission also takes place from below the surface as well as directly from it. Stewart proved experimentally that the radiation from a thick plate (of a body neither black nor transparent) is greater than that from a thin plate of the same substance, both being at the same temperature.

304. A very simple calculation enables us to trace the effect of thickness on the direct radiation from a plate. Let R represent the direct radiation of a definite kind, when the plate is of unit thickness (the unit may be chosen as small as we please), and a the corresponding absorptive power for the same radiation at the same definite temperature. Then a second unit plate of the same substance, at the same temperature, placed in front of the first, and so close as to be virtually one with it, radiates also R, but stops aR of that emitted by the first. The whole radiation from the double plate is thus:—

$$R\,(1 + (1 - a)).$$

A third unit plate placed in front of these contributes R and stops $aR\,(1 + (1 - a))$. Hence the whole effect of three plates is

$$R\,(1 + (1 - a) + (1 - a)^2).$$

The law is now obvious; and, by summing a geometric series, we find for the radiation of a plate n units thick

$$R\frac{1 - (1 - a)^n}{1 - (1 - a)}.$$

However small may be the value of a, provided it do not vanish, $(1 - a)^n$ vanishes when n is infinite. This gives the utmost amount which a mass of the substance can emit, and the value is then

$$\frac{R}{a}.$$

This is, of course, equal to its absorptive power for the corresponding radiation from a black body of the same temperature. Hence if a stand for this perfectly definite quantity, we have

$$R = a\alpha\,;$$

and the preceding expression for the direct emission from a plate of n units thickness becomes

$$a\,(1 - (1 - \alpha)^n).$$[1]

The following little table will be useful in showing the consequences of this expression. It gives the values of the quantity $1 - (1 - \alpha)^n$, the corresponding values of α being in the upper line of the table (*i.e.* the values of the expression for $n = 1$), and those of n in the left-hand column. The numbers in the table may of course be taken as representing the relative absorptions by different thicknesses of the plate. Their defects from unity give the corresponding transmissions:—

1	0·1	0·01	0·001	0·0001
10	0·651	0·096	0·010	0·001
100	0·99997	0·634	0·095	0·01
1000	1·0	0·99996	0·632	0·095
10000	1·0	1·0	0·99995	0·632
100000	1·0	1·0	1·0	0·99995

305. One very remarkable conclusion from the above expression is that a stratum of any substance, however slight its emissivity for particular radiations, will, if only

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[1] The above is not rigorous, but is sufficient for our purpose. To obtain a rigorous investigation we may put α/m for α, and mn for n, and then make m infinite. Or we may proceed as follows:—Let R, α, be such that a plate of thickness δx, at the given temperature, emits $R\,\delta x$ of a particular wave-length, absorbing $\alpha\,\delta x$ of that of the same wave-length, from a black body. Then, if $\phi(x)$ be the whole radiation of that kind from a plate of thickness x, we have at once $\phi(x + \delta x) = (1 - \alpha\delta x)\,\phi(x) + R\,\delta x$, so that $\phi'(x) = R - \alpha\phi(x)$, and $\phi(x) = \frac{R}{\alpha}(1 - \epsilon^{-\alpha x}) = a\,(1 - \epsilon^{-\alpha x})$.

thick enough, behave exactly as a black body. For, in all probability, all actual substances emit, when hot enough, though in very different amounts, every ray. Thus we can understand why the body of the sun, though probably gaseous (the greater part of its materials at all events being at temperatures far above their critical points), radiates as if it were a black body.

Another very important conclusion is that a body, whose absorption is specially and sharply selective, may stop a large percentage of the incident radiation from a black body very early in its career, while the rest may pass through considerable additional thickness with comparatively little loss.

It is quite otherwise with a body whose absorption is not selective, even though it be nearly transparent; such a body, in great thickness, is nearly opaque.

306. From the general statements above, it is clear that experimental determinations connected with this subject may be made either directly on the radiation from a substance, when it is hotter than the surrounding bodies, or indirectly on the radiations which it allows to pass through it from a hotter body.

Such experiments, direct or indirect, are comparatively easy when the radiation is visible, although even then there is one insuperable difficulty, viz., the eye estimation of relative brightness of light of different wave-lengths. This, however, belongs properly to *Photometry*, a branch of practical Optics. We may merely mention that the principle usually employed is that of the law of diminution of intensity of radiation with increase of distance from a point-source (§ 280). The two sources to be compared illuminate each a portion of a screen, and their relative distances from the screen are adjusted till the eye judges these portions to be equally illuminated. But it is quite clear that rays belonging to the middle portion of the range of visible radiation will, by this process, be favoured at the expense of those belonging to the ends of the range.

The same is true of all photographic processes. Each of these, like the eye, has its particular range (sometimes above, sometimes in, and sometimes altogether below, the visible spectrum), the middle part of which it especially favours. In fact, the true use of any photographic process is to detect special regions of very great absorption. The only true method of comparing radiations of very different wave-lengths is to convert them into heat, and measure the amount produced in a given time. This could be perfectly effected if we had bodies such as (6) of § 294, each transparent for one definite group of wave-lengths only, and perfectly reflecting all others; and if we could keep the normal temperature of our pile or thermometer close to absolute zero. These conditions are alike unattainable, so we must employ the least faulty method at our disposal.

307. One such method depends on one of the early results obtained by Young, when he revived Huyghens' *Undulatory Theory of Light*, and developed it by the help of his own doctrine of *Interference*. He showed that if a parallel beam of white light passed from a distant source perpendicularly through the plane of a grating of equidistant parallel wires, and were afterwards received on a screen, the white spot (which would have been formed on the screen had no grating been interposed) would be weakened, and accompanied by a series of coloured spectra. These are arranged symmetrically on each side of the white spot, in a line perpendicular to the wires of the grating. The amount of displacement of any particular colour from the central white spot is very nearly in direct proportion to

the corresponding wave-length. It is also directly as the distance of the screen from the grating, and inversely as the distance between the axes of the successive wires. By adding, after Newton, the refinement of a narrow slit (parallel to the wires) through which the light falls on the grating, and an achromatic lens of long focus between the grating and the screen, the various wave-lengths can be so perfectly separated from one another that the chief Fraunhofer lines are distinctly shown when sunlight is employed.

The distribution of energy in such a spectrum can now be studied directly by means of a thermo-electric pile, whose junctions are all arranged in one line parallel to the wires of the grating. Placed in any position on the screen it gives, by the deflection of the galvanometer, a measure of the amount of energy of the original radiation which is comprised between two wave-lengths differing by an amount proportional to the *breadth* of the face of the pile. The pile can be made to travel, keeping its length parallel to the wires of the grating, all along the spectrum, by means of a screw motion.

308. The objections to this method are very numerous.

(1.) The greatest intensity of the spectral radiation is necessarily only a very small fraction of the whole radiation.

(2.) The lengths of the spectra, so far as visible radiations are concerned, are necessarily very small, because, for our present purpose, we must use actual wires or something equivalent, and we cannot well have more than a hundred or so per inch.

In such a case, even if the slit and the screen were each twenty feet from the grating, the utmost deflection of the red of the first spectrum from the central line would be two thirds of an inch.

[Gratings, such as are employed for optical purposes, may have many thousand lines per inch; but their heat indications must be received with caution, as they are usually formed of lines ruled with a diamond on glass or speculum metal; and the various classes of obscure radiations may be treated very differently (one from another) by passage through glass, or by reflection from metal. Thus, such gratings give perfect indication of intense special absorption (such as the Fraunhofer lines), but require supplementary evidence when they appear to weaken a large region of the spectrum.]

(3.) As the pile deals with *all* radiations, and not merely with those which are visible, the effect upon it in any position is due to a particular wave-length of the first spectrum, radiation of half that wave-length from the second spectrum, &c.

(4.) The statements made above hold only for waves whose length is considerably less than the distance between the axes of successive wires. With longer waves the phenomenon is of a different character.

(5.) The comparison, at different parts of the spectrum, ought to be between groups of wave-lengths whose extreme *ratio* in each group is the same; whereas this method deals with groups in which the extreme *difference* is the same, thus giving the shorter waves an undue advantage.

309. When we try a refraction spectrum, instead of a diffraction one, we are met by a somewhat different, but quite as formidable, array of difficulties. Some of these may probably be got over by the recent improvements in photography, which enable us to utilise the obscure rays of longer wave-lengths than red, just as the old methods employed chiefly obscure rays of wave-lengths shorter than violet.

(1.) We must have independent means of discovering the absorptive power of the material of our prism for each obscure wave-length. We cannot trust even such a substance as rock-salt, without direct proof that it has not some special absorption for a definite region of the spectrum.

(2.) Even supposing we had this, the crowding together, according to an as yet unknown law, of the less refrangible rays, offers a very serious difficulty. With light we know that, to a rough degree of approximation, the refractive index of a transparent body can be expressed by the formula

$$\mu = A + \frac{B}{\lambda^2}$$

where λ is the wave-length, and A and B are special constants for each medium. If this law holds, even approximately, for wave-lengths much exceeding those of visible light, there must be an immense assemblage of radiations for which the refractive index is practically the same; and the intensity of the whole radiation in a given fraction of the length of the spectrum must increase (provided there is no special absorption) steadily to the limit, for which $\mu = A$. But, in practice it has been found impossible to prevent *scattering*, however carefully the substance used as a prism has been selected, and however truly its surfaces have been worked into polished planes.

Again, it must be noticed that what the pile indicates is the excess of the radiation reaching it over that which is leaving it. Thus, all its indications are in defect, and to a greater amount the higher is its mean temperature.

Many more difficulties might be urged, but those specified are sufficient.

310. The remarks just made must have prepared the

reader to find that our positive knowledge on this subject, so far at least as obscure rays are concerned, is of very slender amount; and that even our general information is of a somewhat doubtful character.

Attempts have been made to exhibit graphically the intensity of visible rays at each point of the spectrum. These are all, however, doubtful on account of the difficulty already hinted at (§ 306) of estimating the apparent relative brightness of rays of different colours. There is a general consensus (except with some of the colour-blind), that the maximum is somewhere in the yellow, but (as might be expected) not much farther agreement.

W. Herschel was the first to point out that the hottest part of the solar spectrum (as determined by a thermometer) was, not only not coincident with the brightest part but, situated differently with regard to the visible part according to the material employed as a prism. It is in fact within the visible part when a prism of water is used, but outside it and beyond the red end when the prism is of rock-salt. The reason is obviously the transparency of rock-salt, and the opacity of water, to the obscure radiations.

311. Melloni, Forbes, and others have tried to meet some of the difficulties of this problem in another way, viz. by measuring directly the amount of absorption of any one body for radiations from a series of sources at different temperatures; *e.g.* a Leslie's cube (§ 291), blackened copper at 200° C., 400° C., &c., a Locatelli lamp, a white-hot platinum spiral, &c. But all such observations are seen to be of comparatively little interest when we look at them from the point of view suggested by the behaviour of coloured glass. For there we find that an apparently trivial quantity of foreign matter (cobalt, manganese, gold, &c.) entirely alters the behaviour of the glass as regards visible

radiations. There can be little doubt that this effect extends, to at least as formidable an amount, to the behaviour of bodies with regard to obscure radiations. And this prepares us to expect, what in fact we find, that there can be no close agreement between the results obtained by different experimenters unless they have operated, not only on the same substance, but on the same specimen of the substance, so long at least as it is a natural and not an artificial product.

312. When substances can be obtained chemically pure, we naturally expect a much closer agreement between the independent results of different experimenters. Thus all experimenters seem to agree that water, and aqueous solutions (especially that of alum), are singularly opaque to the lower obscure radiations. There is also a fair agreement as to the behaviour of gases; some (as dry air for instance) being found to exert very slight absorption on obscure rays in general, others (like olefiant gas) being powerful absorbers of such rays. This subject has been elaborately investigated by various experimenters. We are prepared of course to find such differences by our knowledge of the existence of *coloured* gases; such as chlorine, and especially nitrous acid which (as Brewster showed) can be rendered practically opaque to sunlight, even when in small thickness, by being sufficiently heated.

313. But when we come to vapours the question is not by any means so definitely answered. There can be no doubt that even a small amount of water-substance in air considerably increases the absorption of obscure radiations. But we do not yet know whether this effect is general or selective. And more, it has not yet been decisively shown that this effect is wholly due to *vapour* of water. We all know how slight a cloud or fog is sufficient greatly to mitigate

the glare of the sun, while stopping his heat as well as his light. This can be accounted for, to some extent, by the mere reflection, &c., from the small drops of water. But if we were to attempt a rough approximation to the brightness of a cloud in full sunshine by assuming that it sends back to a hemisphere the amount of light which it receives from the sun (a disc of 0°·25 in radius); *i.e.* its brightness would, on this hypothesis, be to that of the sun as 1 : 120,000 nearly. This would be nearly equivalent to assuming that, if the whole sky were covered with cloud as bright as it is in full sunshine, the amount of light we should receive would be the same as that from the direct sun alone. This estimate must be very considerably *above* the truth. For though clouds in sunshine appear brighter than the moon, yet the ratio of full moonlight to sunlight is given by Herschel (after Wollaston) as about 1 : 800,000, only. Thus the amount of sunlight reflected by a cloud must be only about $\frac{1}{5}$ or $\frac{1}{4}$ of the whole. The greater part of the remainder is absorbed.

The direct heat-radiation from the sun is felt powerfully even when the air appears to be saturated with moisture; as in the intervals between heavy showers, the "clear shining after rain." But the showers have extracted, at least in great part, the dust nuclei which are required for condensation (§ 176); and it would appear that such saturated air, if only supplied with a little dust, would at once become practically opaque to sun-heat by the formation of mist or clouds. Still, we must also bear in mind that a rain-cloud is the summit of an ascending column of warm, moist air, and *therefore* the interval between two clouds is in great part a descending column of drier air.

314. The absorption due to true water-vapour, both as to quality and as to quantity, has been a specially vexed question for the last twenty years, and still remains

unsettled. All that can yet be definitely said on the subject is that, for obscure radiations as a whole, true water-vapour is certainly much more transparent than olefiant gas, and is possibly much less transparent than dry air. Its main absorption is probably for certain *definite* obscure radiations. This question may possibly admit of solution by the recent invention of Abney, which gives the means of photographing the obscure radiation. Had steam an absorptive (and therefore a radiative) power at all approaching to that of olefiant gas, there would be practically no difference in the amount of dew after a clear night and after a cloudy one: for, if the night were clear and the air nearly dry, there would be considerable cooling of the ground, but little dew to fall—and, if the air were moist, there would be material for dew but little cooling to precipitate it. Practically, the results of Wells are independent of the absorption due to true water-vapour.[1] The great difference between the effects of true water-vapour and cloud or mist is seen at once by any one who watches the puffs of steam from a locomotive. These are practically transparent for the first few feet above the funnel, but become almost absolutely opaque when condensation takes place.

315. There is yet another class of phenomena, already referred to, which claims mention here, though (from its very nature) it has hitherto been observed only in connection with visible radiations, and therefore is more properly treated in works on *Light*. This is designated by the terms *Fluorescence* and *Phosphorescence*, which are probably mere varieties of one phenomenon.

By *Phosphorescence* is meant something very different from the luminosity (in the dark) of a stick of phosphorus or a line drawn with it on a wall, of decaying wood, or of

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[1] W. Thomson, *Proc. R.S.E.*, v. 203 (1864).

dried fish. These probably depend upon slow oxidation, or other chemical combination, and therefore belong to combustion; though, in some special cases, they are known to be due to colonies of bacteria. But it was known to the ancients that certain gems, after being heated, continue luminous in the dark long after they have cooled down to the temperature of the air. The properties of the Bologna stone (sulphide of barium) were discovered in the seventeenth century, those of Canton's phosphorus (sulphide of calcium) in the eighteenth. And now we have many varieties of chlorides, sulphides, &c., which, like these preparations, shine brilliantly in the dark for hours after they have been exposed to sunlight or to a burning magnesium wire. Recently these bodies have been applied to various purposes as the bases of *Luminous Paints.* The curious property exhibited by them is correctly called Phosphorescence.

Certain crystals of greenish Fluor-spar, a piece of canary glass (coloured with oxide of uranium), a decoction of horse-chestnut-bark (esculine), and a slightly acidulated solution of sulphate of quinine, show each a peculiar surface colour of its own even in ordinary daylight, much more strongly in sunlight or electric light. A brilliant investigation by Stokes, in 1852, showed that this was due to the giving out, as altered light, of light absorbed by the body: in fact, Stokes's paper has the title *On the Change of Refrangibility of Light.* This is correctly called Fluorescence. It appears that in all cases the wave-length of the emitted rays is greater than that of the rays absorbed.

Fluorescence appears to differ from true Phosphorescence mainly in being of very much shorter duration. But we must refer to works on Light for the description of the Phosphoroscope, and the results obtained by its use.

316. The mechanism by which this apparent storage and subsequent doling out of light are produced is still

somewhat obscure, and the hypotheses which have been advanced by Stokes and others are too difficult to be treated here, especially from the point of view of the general proposition (§ 295).

We merely refer again to the serious limitations (§ 292) under which the whole theoretical part of this subject admittedly still lies; and point out the apparent inconsistency which appears between the two statements : (*a*) that the emission of any particular radiation by a given body depends on its temperature only, increasing in intensity as the temperature rises; and (*b*) that certain fluorescent bodies give out visible radiations at temperatures at which even a black body would emit obscure radiations only.

317. *Résumé* of §§ 288–316. Prevost's Theory of Exchanges. Radiation as depending on Nature of Surface. Extension of Prevost's Theory. General relation between Emissivity and Absorptive Power. Physical Analogy. Spectrum Analysis. Internal Radiation. Absorption by plates of different thickness. Distribution of Energy in the Spectrum. Absorption by gases and vapours. Fluorescence and Phosphorescence. Defects in the Theory.

CHAPTER XVIII.

RADIATION.

318. So far we have been dealing mainly with the relations between the absorptive and emissive powers of a body, or bodies, at one definite temperature. And we have had, to some extent at least, the help of theoretical considerations.

But we must appeal directly to experiment for information as to the comparative amounts of emission or absorption by the same body *at different temperatures*, whether these refer to the radiations as a whole or are confined to one particular wave-length. Mechanical analogies, which were of considerable assistance in the former part of the work, fail us here because of our ignorance of the nature of the vibrations of the particles of a hot body, and of the mode in which their energy is transferred to the ether. All that we have yet arrived at, in this connection, is that a rise of temperature in the radiating body is accompanied by an increase of emissive power for each kind of radiation. Whether this is nearly the same for different wave-lengths or not, we have had as yet no information.

319. It must be remembered that we are now dealing with emission alone; not with the whole radiation, which, as we have seen, is the same for all bodies in our imaginary

inclosure. With black bodies this is wholly emission, but with other bodies it is partly emission, partly transmission, and partly reflection. For simplicity we will, therefore, at first confine ourselves to black bodies. And, for comparison with Prevost's Theory of Exchanges (§ 290) we will suppose that our inclosure contains two black bodies at different temperatures, and these only. Farther, to approximate as nearly as may be to a case realisable in actual experiment, we will suppose that the colder black body *lines* the inclosure, while the hotter is suspended within it. This is nearly realised in the case of a thermometer, with a very large blackened bulb, inclosed in a receiver blackened internally and exhausted of air—a form of experiment which is easily carried out. To avoid the difficulties of convection currents, &c., in the liquid filling the bulb, we may suppose the blackened body to be a large solid ball made of a good metallic conductor, with a hole in it containing mercury, into which the bulb of an ordinary thermometer is inserted; the stem of the thermometer passing air-tight through the inclosure. If the inclosure be also of good conducting metal, we may suppose it to be kept at a constant temperature by immersion in a large vessel full of water, which is constantly renewed from a cistern. The ball is heated, once for all, inserted with the thermometer in the inclosure, and the vacuum made as speedily as possible. The readings of the thermometer are then taken (as in § 180) at intervals of a minute. The water-equivalent of the ball, mercury, and thermometer-bulb together are found by the proper methods, and enable us to calculate the number of units of heat lost for the fall of temperature observed. This number, divided by the number of square units in the surface of the ball, gives the loss of heat by emission per unit of surface, per minute, at each temperature.

320. If the absolute temperature of the ball be t, and that of the inclosure t_0, and if $f(t)$ represent the rate of surface-loss per unit surface at temperature t, the quantities thus calculated from the results of experiment are the successive values of

$$f(t) - f(t_0).$$

321. The earliest speculations on the subject, including those of Newton, assumed that this quantity is proportional simply to the difference of temperatures

$$t - t_0,$$

so that, for all temperatures,

$$f(t) = A\,t + B,$$

where A and B are constants. This is the assumption made (even when convection also comes into play) in all the theoretical writings of Fourier. And it is found to be approximately true so long as the temperature-differences are not above a few degrees.

322. Dulong and Petit, by a very careful series of experiments, found that this approximation errs in defect, even for moderate temperature-differences, and that the percentage of error rapidly increases as these differences increase. But they found that the results of all their experiments, up to temperature-differences of 200° C. at least, when the inclosure was at temperature from 0° up to even 80° C., could be well represented by an exponential formula of the form

$$f(t) = A\,a^t + B.$$

The quantity A was found to depend upon the nature of the radiating surface only; while $a = 1{\cdot}0077$, is, according to these experimenters, practically the same for all bodies. [B, of course, cannot be found experimentally:—but should be equal to $-A$ if this formula were true for all temperatures down to absolute zero, for there obviously can be no radiation when $t = 0$.]

323. De la Provostaye and Desains have verified the consequences of this formula from 0° C. to 200° C.; but they state that above the latter temperature it is no longer applicable.

The simplicity of this expression, especially as α was found sensibly the same whatever was the nature of the emitting surface, might lead us to fancy that it might be obtained as a consequence of theory, but we have as yet no information about the mechanism of emission on which to base a theory.

324. Accepting it, however, as a fair approximation to experimental results between the limits assigned above, we find for the rate of surface-loss

$$f(t) - f(t_0) = A\,\alpha^{t_0}(\alpha^{t-t_0} - 1).$$

Thus we have the approximate statements:—

For a given temperature of the inclosure, the rate of surface loss is proportional to

$$(1{\cdot}0077)^{\theta} - 1$$

where θ is the difference of temperatures in degrees C.

For a given difference of temperatures the rate of surface loss is proportional to

$$(1{\cdot}0077)^{t_0}$$

where t_0 is the absolute temperature of the inclosure.

It therefore rises, in geometrical progression for equal increments of temperature.

325. The first of these results shows that the rate of cooling, for moderate temperature-differences, is proportional to

$$\theta\,(1 + 0{\cdot}0038\,\theta + \&c.).$$

from which we see the nature of the approximation in what is called Newton's Law. The error is about 4 per cent., in defect, for a temperature difference of 10° C.

We have no very definite information as to the actual value of the quantity *A*. According to the experiments of Hopkins, it is about $\frac{1}{6}$th of a unit of heat per minute, per square foot, from a surface of glass. From this it follows that the radiation from glass at 100° C. to an inclosure at 0° C. is about one unit of heat per square foot per minute.

326. Though the law of Dulong and Petit is found to hold approximately for a considerable range of temperature, and for surfaces of all kinds, it does not appear to hold even approximately for each separate wave-length. If it did so, the *character* of the radiation from a black body (*i.e.* the proportions in which its whole energy is distributed among the various separate wave-lengths) would be the same throughout that range of temperature. Thus the percentage absorption by one and the same body would be the same for radiations from all black sources at temperatures within that range. This is at variance with the great majority of Melloni's results. Thus he found for the percentage absorption of heat from different sources by plates of equal thickness at ordinary temperatures:

	Blackened Copper		Platinum	Locatelli
	at 100 C.	at 400 C.	incandescent.	lamp.
Rock-salt	8	8	8	8
Fluor spar	67	58	31	22
Iceland spar	100	94	72	61
Alum	100	100	98	91

We have added, for comparison, two other sources, of which one at least is certainly not a black body.

327. Even a brief table like this seems to prove beyond all doubt (at least so far as the theoretical conclusions of

Chapter XVII. may be trusted), that the amount of emission of any particular radiation by a black body increases, after being first perceptible, more and more rapidly as the temperature is raised, thenceforward more and more slowly as it is still farther raised.

[A desideratum, which could easily be supplied with modern apparatus, is a careful series of experiments like those of Melloni, made with the same blackened body as source, but taken successively at temperatures 50°, 100°, 150° . . . 500° C higher than the absorbing plate and the pile. Such a series, for each of a well-selected set of absorbing plates, would be of high scientific value.]

328. We must here mention a very curious speculation (due to Balfour Stewart) which, possibly from some inaccuracies involved in the first statement of it, does not seem to have met with the consideration it certainly merits. It is based on what is called *Döppler's Principle*, which is merely an application of the reasoning by which Römer first measured the velocity of light.

329. If a periodic disturbance of any kind (producing water-waves, sound-waves, light-waves, &c., propagated at a uniform rate), take place at a centre, the *number* of these disturbances which reach a spectator in a given time depends on his relative velocity with regard to the centre. When he is approaching it they are more, and when he is receding from it less numerous, than if he were at relative rest. We are not, however, entitled (without proof) to assume that the result will necessarily in all these cases be *precisely* the same as if the spectator and the centre had been at relative rest, while the period of the original disturbance was shortened or lengthened. To show the necessity for caution in this matter, let us suppose both centre and spectator to be at rest, but the wave-medium to

be moving from one to the other. In this case the waves will be lengthened or shortened, but their rate of propagation will be proportionally increased or diminished, so that the number received in a given time remains unaltered.

But experiments on musical sounds produced by a trumpeter on a passing train have verified the principle for sound ; and it has also been, to a certain extent, verified for light by the observed difference of refrangibility of definite lines in the solar spectrum according as the light comes from the east or west limb of the sun. [The east side is approaching us, and the west side receding from us, in consequence of the sun's rotation, at such a rate that while 150,000 light waves of any species are given off, there reach us about 150,001 of the same species from the east side, and 149,999 from the west. Thus, if the spectra of these two sources of light be formed side by side by the same prism, the Fraunhofer lines in the two will not coincide. The relative displacement of each in the two spectra will be as if one had a wave-length about $\frac{1}{75000}$th greater than the other.] A similar agreement with theory has been obtained with the light reflected from Venus. This principle has been successfully applied by Huggins and others to find the proper motions of the stars in the direction of the line of vision. Thus it is (so far) proved that radiation from one body to another depends upon their relative motion only, and not upon the motion of the ether relative to either of them.

330. Assuming, then, the principle to be accurate (as it is at least partially verified by experiment) if in our inclosure (§ 295) one of the bodies is moving relatively to the others, the only way in which we could conceive equality of temperature to be maintained would be by supposing the energy corresponding to each of the infinite variety of

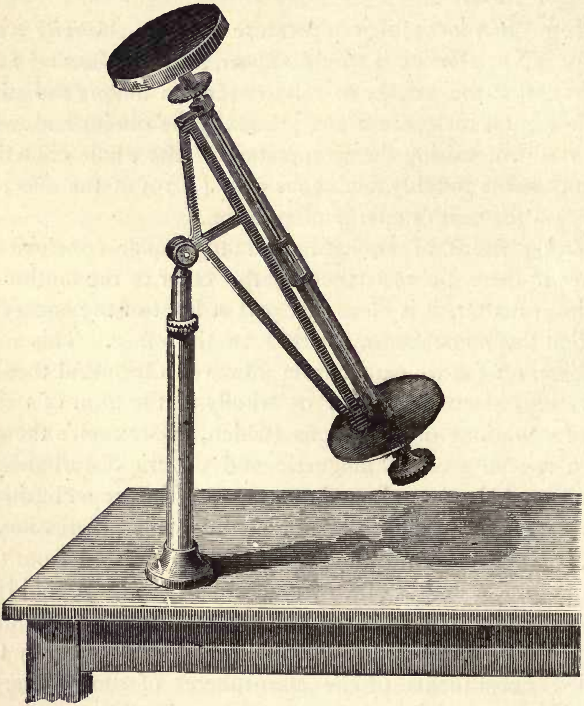
wave-lengths in the radiation from a black body to be of the same amount at any one temperature. This is certainly not the case; and therefore, if our assumption is correct, it follows that *relative motion of radiating bodies in an inclosure is inconsistent with ultimate equality of temperature amongst them.*

Now differences of temperature involve *Motivity* (see Chap. XX). Hence it would appear, from the Second Law (§ 82), that the energy of relative motion among radiating bodies in an inclosure must gradually be diminished, with the result of raising the temperature of the whole contents. Compare the roughly analogous case (§ 70) of the effect of tides on the earth's energy of rotation.

[Other trains of thought lead to similar conclusions. Thus, if there be resistance by the ether to the motion of ordinary matter, it is clear that part at least of the energy of motion lost must be transferred to the ether. This may be given off (as we gather from Maxwell's beautiful theory) in various electrical forms, or wholly in the form of transverse vibrations or radiations (which, in Maxwell's theory, are a special case of magnetic and electric disturbances). But it would lead us altogether away from the proper business of a text-book to pursue this highly interesting digression.]

331. The absolute amount of energy radiated from the sun is to us a matter of truly vital importance. It could be determined with great ease, and with considerable accuracy, were it not for reflection, absorption, and scattering, by the various constituents of the atmospheres of sun and earth. But it is not probable that we shall soon be able to estimate even roughly the effect of the sun's atmosphere; nor is it, for our present purpose, of much consequence that we should. What we are most concerned with is *how much radiant energy reaches the earth* in a given time.

Pouillet was the first who made a successful attempt to answer this question; and his results have not been much altered by farther research. The ingenious and simple instrument he devised for the purpose is called the *Pyrheliometer.*



332. It consists essentially of a short but wide cylindrical vessel constructed of highly-polished metal, one end only being covered with lamp-black. This is filled with water or mercury, and immersed in the liquid is the bulb of a

thermometer, whose stem protrudes along the axis of the cylinder. A circular metallic disc, equal in diameter to the cylinder, is supported at the other extremity of the stem. When the instrument is turned so that the shadows of the cylinder and disc coincide, we know that the blackened end of the cylinder must be turned exactly to face the sun. The water-equivalent of the cylinder and its contents, and the area of the blackened end, must both be carefully determined.

Suppose the instrument, at the temperature of the air, to be shaded from the sun, and turned towards the sky. The thermometer will after five minutes show a definite fall of temperature, say t_0.

Now turn the instrument towards the sun for five minutes, let us say. The thermometer rises through t. Turn it immediately to the sky, shaded as before, for five minutes. The temperature falls through $t_,$.

During the time of its exposure to the sun, its temperature was steadily rising by solar radiation, but as steadily falling by its own radiation. Hence we conclude approximately that it lost in temperature by cooling to the amount

$$\frac{t_0 + t_,}{2}.$$

In fact, we take the mean of the two coolings, before and after exposure to the sun, as the cooling during that exposure.

Thus the full gain from the sun would have raised it in five minutes by

$$t + \frac{t_0 + t_,}{2}.$$

From this, and the numerical data for the instrument (which we have specified above), we calculate at once how many units of heat, per unit of surface, have been received from the sun per minute.

333. From a great number of experiments with this instrument, Pouillet concluded that the rate of rise of temperature due to direct solar radiation in a given time, at different hours of the same day, could be represented very closely by an expression of the form

$$A\,e^{\tau},$$

where A and e are constants, and τ represents the length of the course of the rays through the atmosphere, as depending on the sun's altitude.

A was found to be sensibly the same for all the days of observation, but e (which is of course less than unity) varied in a marked manner from day to day.

Pouillet considered that these facts warranted his assuming that the formula would hold good even if there were no atmosphere; in which case we should have $\tau = 0$, and the expression for the rate of rise of temperature would be A simply.

Thus he calculated from the data of his instrument that the amount of heat which in one minute would reach directly a square centimetre of the earth's surface, if there were no atmosphere, would raise the temperature of 1·76 grammes of water by 1° C. In the units we have hitherto employed this is about 3·6 units of heat per minute, per square foot of surface. From this it can be easily calculated that the total heat received from the sun in the course of a year would, if distributed uniformly over the earth, be capable of melting a crust of ice somewhere about 95 feet thick.

334. From the average values obtained for the quantity e in his formula, Pouillet concluded that, when the sun is

vertical and the sky clear, from eighteen to twenty-five per cent. of the solar heat is absorbed before reaching the earth; and that (taking obliquity into account) half of the entire heat which comes from the sun to the illuminated hemisphere of the earth is absorbed by the atmosphere. Forbes's experiments on the Faulhorn showed that on the clearest days the lowest 6,000 feet of the atmosphere absorbs one-fifth of the radiant energy received from the sun.

335. The earth, as seen from the sun, is a disc occupying only about $\frac{1}{2300000000}$ of the surface of the celestial sphere. Hence we can calculate (assuming it to be uniform) the amount of heat lost by each square foot of the sun's surface in a given time. W. Thomson, using (along with Pouillet's just given) the data of Herschel, finds that the sun's radiation is at the rate of about 7,000 horse-power per square foot, about thirtyfold that of the same area of the furnace of a locomotive. Also that the whole heat which leaves the sun per annum is about 6×10^{30} units C.

All these estimates, however, though they are almost certainly of the proper *order* of magnitude, must be looked on as mere approximations.

336. The great majority of the experimental determinations of absolute rate of loss of heat have been made in air, so that convection as well as emission has a share in the effect.

Here, again, Dulong and Petit furnish us with an empirical law. They find that the convection effect is entirely independent of the radiation; and is the same at the same temperature for a particular body, whether the surface be polished or blackened. It depends, of course, upon the nature of the surrounding gas, and upon its pressure (p) as well as upon the temperature excess of the body. This part of the loss of heat can, they find, be expressed in the form

$$A\,p^{\beta}\,(t - t_0)^{1\cdot233}.$$

Here A is a special constant; and β varies from one gas to another, being about 0·45 for air.

These experiments were made with an apparatus such as that described in § 319 above, which could be filled, at pleasure, with any gas at any desired pressure. The law to which they led has, however, been shown by De la Provostaye and Desains to be only roughly approximate. Especially is this the case for low pressures, when the inclosing vessel is small.

337. Determinations of absolute amount of loss by radiation and convection together are not numerous. We may cite the following, due to Nicol:—

Loss in heat units, per square foot, per minute, from

Bright Copper	1·09	0·51	0·42
Blackened	2·03	1·46	1·35

Here the hot body was 50° C. above the inclosure at 8° C., and the pressure of the contained air was, in the three columns, about 30, 4, and 0·4 inches of mercury respectively.

According to Macfarlane's experiments, the numbers in the first column should be 1·38 and 2·01 respectively. But in this case the temperature of the inclosure was 14° C., and the air was saturated with water vapour.

The agreement is very satisfactory, since there can be no doubt that differences in the amount of polish for the bright surfaces, and in the quantity and quality of the material used to blacken them, are capable of accounting for much larger discrepancies.

338. Experiments with the short bars as in Forbes's conduction method (§ 244), give us valuable information of this kind through a much wider range of temperature; though the bars are simply exposed in a room—not in an internally blackened inclosure; while the circumstances must be different for the vertical and the horizontal faces of the bar. The following rough numerical values have been arrived at in this way. The numbers are in the same units as those just given, the air temperature being 17° C.

Temperature Excess.	50° C.	100°.	150°.	200°.	250°.
Polished iron . . .	1·13	2·76	4·76	7·33	10·55
Iron smoked . . .	1·40	3·64	6·75	11·25	17·21

In reducing the experiments, it has been assumed (as in § 247), that the specific heat of iron increases by about 1 per cent. for 7° C. And we observe the curious fact that the ratios of these numbers at each step, of the arithmetical series of temperatures, form almost an exact geometric series.

Though not very concordant, these various estimates give us at least a general idea of the *order* of magnitude of the loss in heat units of a cooling body.

339. *Résumé* of §§ 318–338. Radiation from the same body at different temperatures. Dulong and Petit's Law. Melloni's measures of absorption. Pouillet on Solar Radiation. Pyrheliometer. Loss of heat by radiation and convection jointly.

CHAPTER XIX.

UNITS AND DIMENSIONS.

340. No one has the least difficulty in apprehending that half-a-crown is thirty pence, or that a furlong is 220 yards, or 660 feet. A process precisely similar to that which is really involved in such every-day transformations would enable us to express a given sum of British money in its equivalent in francs, or a number of yards in the equivalent in centimetres. We have already (§ 132), in showing how to transform from one thermometer scale to another, said all that is necessary on the principle of such simple transformations, where we reduce from a mere multiple of one unit to the corresponding multiple of another of the same kind. When two or more units have to be simultaneously changed, the operation is (numerically) somewhat more complex, but the principle is the same. In fact, we might apply it directly by the more laborious process of changing one unit at a time till we had got through the list. Thus a speed of 10 feet per second is 5,280 feet in 528 seconds, *i.e.* a mile in 528 seconds, or (finally) a mile in 8m. 48s. Or we might put it as 600 feet per minute; that is, 36,000 feet, or about 6·82 miles, per hour. Such things present only possible labour, but no difficulty of *principle*.

341. The case is somewhat less easy when we take such a question as this :—The intensity of gravity is represented by 32·2 in feet and seconds, what is it in miles and hours? [We might have desired it in centimetres and minutes, but that would only have altered the necessary numerical factors; leaving the principle of the process unchanged.] In attacking such a question, we must begin by carefully investigating *how the various units are involved.* Once this is done, the rest is mere ordinary arithmetic. Now the meaning of the above statement is that gravity produces in a falling body, in each second, an additional speed of 32·2 feet per second. Notice that the *foot* is mentioned only once, while the *second* occurs twice, in this amplified statement. A little thought will show that, so far as the unit of length is concerned, the numerical expression for the value of gravity must be 5,280 times greater in terms of feet than in terms of miles. Again, the effect of gravity in an hour must be 3,600 fold of what it is in a second; and if we measure this by the space passed over in an hour, instead of that passed over in a second, the result will again be increased 3,600 fold. Altogether, then, we must multiply the given number, 32·2, *twice* over by 3,600, and divide the result by 5,280. We thus obtain for gravity, in miles and hours,

$$32{\cdot}2\,\frac{(3600)^2}{5280} = 79{,}036 \text{ nearly.}$$

That is, a body falling under [constant] gravity acquires, in each hour, an additional speed of 79,036 miles per hour.

342. Look on these two examples from another point of view. Speed is greater as the space passed over is greater, and less as the time employed is greater. Hence

it involves length directly, and time inversely; or as it is the custom to write it,

$$[\mathbf{V}] = \left[\frac{\mathbf{L}}{\mathbf{T}}\right]$$

But acceleration is greater as the additional speed produced is greater, and less as the time employed in producing it is greater : thus

$$[\mathbf{A}] = \left[\frac{\mathbf{V}}{\mathbf{T}}\right] = \left[\frac{\mathbf{L}}{\mathbf{T}^2}\right].$$

Now, when a unit is increased in any proportion, a concrete quantity, expressed in terms of it has its numerical value diminished in the same proportion. [Thus when we increase the unit twentyfold, as in passing from shillings to pounds, we find 480*s.* = $\frac{1}{20}$ 480*l.* = 24*l.*] Every definite quantity is homogeneous in terms of each fundamental unit it involves. Thus in the expression for the space described under constant acceleration in the line of motion, we have

$$s = a + bt + \tfrac{1}{2}\,ct^2.$$

Here s and a are each of dimensions $[\mathbf{L}]$

b, a speed, is . . . . . . $\left[\frac{\mathbf{L}}{\mathbf{T}}\right]$

and c, an acceleration . . . . $\left[\frac{\mathbf{L}}{\mathbf{T}^2}\right]$

Thus each term of the value of s is, like s itself, of the dimensions $[\mathbf{L}]$.

Hence it appears that, to determine the numerical factor required to pass from any one system of units to another, all that is required is to *find the dimensions of the quantity we are measuring, in terms of the fundamental quantities*, to one or more of which every other measurable quantity can always be referred. As already remarked, the theory of dimensions is due to Fourier.

343. The fundamental quantities are length [**L**], mass [**M**], and time [**T**], and it is a matter of mere convention what amounts of these we shall assume as our units.

Thus we may employ, as we have hitherto done, a foot-pound-minute system; we might adopt a mile-ton-day system; or, what seems to be in a fair way towards adoption in science, a centimetre-gramme-second (C. G. S.) system.

The student must remember that the choice of units is in no way whatever of scientific importance, being a matter mainly of convenience: what is really wanted for science is a *general* system, even if it be inconvenient for mere business purposes. (See again, § 56.)

344. But the question of dimensions is of the utmost scientific importance, and is too apt to be lost sight of in the contest about units. It would be, perhaps, too much to say that an ill-chosen system of units, which should force a man to *think*, would be preferable to a well-chosen system, likely to cause error by inspiring a blind, mechanical confidence. Still, there is some force in such arguments. Spelling and composition are altogether independent of the form of handwriting one employs. But one must know spelling and grammar before he can write correctly, even in the best of "hands." And the unfortunate advocating of the C. G. S. system, under the specious denomination of *Absolute Units*, is very apt to mislead the beginner, by giving him the impression that this choice of units has some mysterious connection with the truths of science. If a proposed system of units were more handy for general purposes than those which they are designed to supersede, every one would cry out for a change. It is undoubtedly on the score of general convenience that our present standards

have come into use. Every one knows what is meant by a man of five feet eight, who "scales" twelve stone. In the C. G. S. system this advantage is wholly sacrificed for the sake of another advantage (felt especially in electrical measurements). The average height of a man, and his ordinary walking pace, are here each expressed by about 170 of the proper units; his mass is somewhere about 70,000 units; while his weight, also in the proper unit (*dyne*), approaches the gigantic figure of 70,000,000. A horse-power is about 7,500,000,000 *ergs* per second. Thus the system is not likely to be employed for any but strictly scientific purposes.

[A much more imperative want, of the same kind, is a common *language* of science. If *original* works were now, as they used to be, written in Latin—how much more rapidly would not science progress? No doubt most of the new and valuable scientific work of the day is published in English, French, or German; or at least given in abstract in some one of these languages. But there is much of it left imbedded in Czech, Danish, Dutch, Italian, Russian, Swedish, &c., and thus practically lost to the great majority of those to whom it might be of the utmost importance. The wise conservatism of the botanists, much as it is ridiculed by "advanced" science, has preserved to them this invaluable system of freemasonry.]

345. The following statements of dimensions are self-evident:—

Volume $[\mathbf{v}] = [\mathbf{L}^3]$. Speed $[\mathbf{V}] = \left[\frac{\mathbf{L}}{\mathbf{T}}\right]$.

Density $[\rho] = \left[\frac{\mathbf{M}}{\mathbf{L}^3}\right]$. Momentum $[\mu] = \left[\frac{\mathbf{ML}}{\mathbf{T}}\right]$.

Force $[\mathbf{F}] = \left[\frac{\mu}{\mathbf{T}}\right] = \left[\frac{\mathbf{ML}}{\mathbf{T}^2}\right]$.

Pressure $[\mathbf{p}]$ = force per unit surface = $\left[\frac{\mathbf{F}}{\mathbf{L}^2}\right] = \left[\frac{\mathbf{M}}{\mathbf{LT}^2}\right]$.

Energy $[\mathbf{E}] = [\mathbf{FL}] = [\mathbf{MV}^2] = [\mathbf{pv}] = \left[\frac{\mathbf{ML}^2}{\mathbf{T}^2}\right]$.

Power $[\mathbf{P}] = \left[\frac{\mathbf{E}}{\mathbf{T}}\right] = [\mathbf{FV}] = \left[\frac{\mathbf{ML}^2}{\mathbf{T}^3}\right]$.

346. We now come to complex dimensions specially connected with our subject. And here a new fundamental unit, temperature $[\Theta]$, is required. This, again, is optional, but we may take it for illustration as 1° C. on the absolute scale (§ 96).

A few instances, fully worked out and explained, will show the reader the principles of this subject; and he may then easily work out the other cases for himself.

The co-efficient of dilatation (§§ 100, 113) is the ratio of the fractional change of length or volume to the corresponding change of temperature. The fractional change is a mere number, so that the dimensions of expansibility are simply

$$[\Theta^{-1}].$$

Heat, $[\mathbf{H}]$, as we have seen, may be measured in many ways. If it be measured in dynamical units, its dimensions are those of $[\mathbf{E}]$ above.

If it be measured in thermal units, *i.e.* by the rise of temperature it produces in a mass of some standard substance (as of water, § 55), its quantity is proportional to the mass and to the rise of temperature, and its dimensions are therefore

$$[\mathbf{M}\Theta].$$

But if it be measured in thermometric units (§ 246) it is of the order

$$[\mathbf{L}^3\Theta].$$

Now by the definition of thermal conductivity (§ 237), we see that

Conductivity × Gradient of temperature × Surface × Time is the measure of the heat which has passed. Thus if k denote thermal conductivity

$$[\mathrm{k}]\left[\frac{\Theta}{\mathrm{L}}\right][\mathrm{L}^2][\mathrm{T}] = [\mathrm{H}],$$

or

$$[\mathrm{k}] = \left[\frac{\mathrm{H}}{\Theta\mathrm{LT}}\right]$$

$$= \left[\frac{\mathrm{ML}}{\Theta\mathrm{T}^3}\right] \text{ in energy,}$$

$$= \left[\frac{\mathrm{M}}{\mathrm{LT}}\right] \text{ in thermal units,}$$

$$= \left[\frac{\mathrm{L}^2}{\mathrm{T}}\right] \text{ in thermometric units.}$$

Similarly we find that

$$\text{Rate of Emission} = \left[\frac{\mathrm{H}}{\mathrm{L}^2\mathrm{T}}\right]$$

$$= \left[\frac{\mathrm{M}}{\mathrm{T}^3}\right] = \left[\frac{\mathrm{P}}{\mathrm{L}^2}\right] \text{ as energy,}$$

$$= \left[\frac{\mathrm{M}\Theta}{\mathrm{L}^2\mathrm{T}}\right] \text{ in thermal units,}$$

$$= \left[\frac{\mathrm{L}\Theta}{\mathrm{T}}\right] \text{ in thermometric units.}$$

347. Thus, to turn the results of § 246, which are in thermal foot-pound-minute units, into the corresponding expressions in C. G. S. units, we have as above

$$[\mathrm{k}] = \left[\frac{\mathrm{M}}{\mathrm{LT}}\right].$$

But

One pound = 453·6 grammes, nearly,
One foot = 30·48 centimetres, „
One minute = 60 seconds.

Hence the factor required is—

$$\frac{453{\cdot}6}{60 \times 30{\cdot}48} = \frac{1}{4{\cdot}03} \text{ nearly.}$$

Thus in C. G. S. units the thermal conductivity of iron is about 0·2, and that of copper from 1 to 0·5.

Again for rate of emission, as in § 337, we have as the reducing factor

$$\left[\frac{M\Theta}{L^2T}\right].$$

Here [Θ] is a centigrade degree in both systems, so that the requisite factor is

$$\frac{453{\cdot}6}{60 \times (30{\cdot}48)^2} = \frac{1}{123} \text{ nearly.}$$

Similarly, and with equal ease, the reducing factor from any one system to another can be found for the other experimental data of our subject.

348. *Résumé* of §§ 340–347. Change of units is a mere arithmetical operation. The real difficulty lies in ascertaining how the various units are involved. Objection to the term *Absolute* Units. Dimensions of Volume, Pressure, Energy, &c. Of Heat, Conductivity, Rate of Emission, &c. Examples of reduction to C. G. S. units.

CHAPTER XX.

WATT'S INDICATOR DIAGRAM.

349. Besides the many capital improvements which Watt introduced into the steam engine [some, such as the separate condenser or the expansive action, being applications of physical knowledge, others, such as the parallel motion, being applications of mechanical ingenuity] we owe to him what is called the *Indicator Diagram*, which is of the utmost importance to the elementary exposition of the fundamental principles of Thermodynamics. Watt devised it for the purpose of determining the work done by a steam engine; and it is still employed for that and similar purposes. But in the hands of Clapeyron, and more recently of Rankine, its properties have been so fully developed that we can represent by means of it not merely the work done by an engine, but the various stages of the process; the thermal properties of the working substance itself; and their connection with the laws of Thermodynamics. The germs of the method indeed are to be found in various parts of the *Principia*, wherever Newton had to represent graphically what we now call an integral.

350. It would be inconsistent with our plan to enter into the practical details of construction of the *Indicator* itself, of which many ingenious forms are in use. These, as well as the details of construction of steam engines, &c., belong

rather to engineering than to physics proper; and can be far more successfully studied by careful examination of the working instrument than by reading descriptions ever so minute, or inspecting drawings ever so accurate. All we need do is to explain the principle involved. And it is simply this: A pencil is so attached to the piston-rod of the engine, that it shares the to-and-fro motion of the piston, and its consequent position at any instant thus indicates the *volume* of the contents of the cylinder. The pencil, however, has another motion, in a direction perpendicular to the first, such that its displacement in the new direction is, at every instant, proportional to the *pressure* of the contents of the cylinder. Thus, as the pencil-point moves over a fixed sheet of paper, it traces a line, every point of which represents a pair of simultaneous values of volume and pressure of the working substance. [In some forms of the instrument, the pencil has one of the two motions, and the paper the other. Also, it is usual to make the adjustments so that the volumes and pressures are represented on a conveniently reduced scale. But the final result is the same: the mode of attainment being mere matter of ingenuity or convenience.]

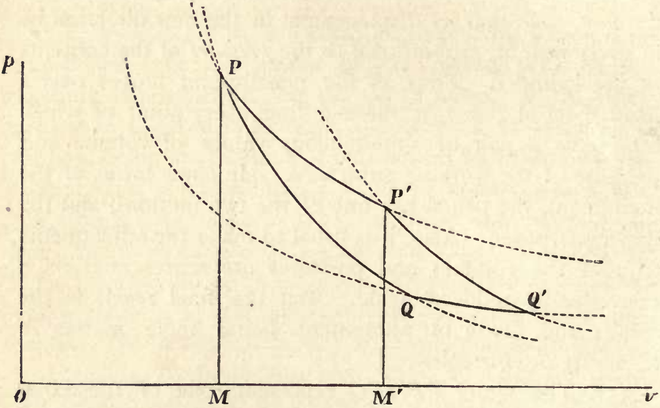
351. The figure $PP'Q'Q$ represents one of these diagrams. The various values of OM represent the volume of the working substance, the corresponding values of MP its pressure.

From Watt's point of view, the diagram gives the work done during a stroke of the engine. In fact if S be the area of the piston, and p the pressure (understood as pressure on unit surface) the whole force exerted is pS. If then the piston move under the action of this force through a space h, the work done is (§ 13)

$$pS.\,h \quad \text{or} \quad p.\,Sh.$$

But Sh is the increase of volume of the working substance. Hence, when the pressure is constant, the work done is the product of the pressure by the increase of volume. This would be the case in the figure, if PP' were a straight line parallel to Ov, and then the work during the expansion from OM to OM' would be represented by the area of the rectangle $MPP'M'$.

When the pressure is (as in the figure) not uniform, we must break up the expansion into separate stages, each corresponding to an infinitesimal change of volume. We thus obtain (as in § 190) a number of narrow rectangles, the sum of whose areas is ultimately the curvilinear space $MPP'M'$. Similar constructions must be made for the expansion from P' to Q' and the contractions from Q' to Q and from Q to P.



If the volume diminish instead of increasing, the work, estimated as before, must be regarded as *spent upon* the working substance, and therefore reckoned as negative.

Bearing this in mind, we see at once that if the closed figure $PP'Q'Q$ be the diagram of an engine, its area represents the work given out during a complete cycle. For the work is positive from P to P', and from P' to Q'; but negative from Q' to Q, and from Q to P.

The work done on the whole, in any such cycle, is therefore positive if the pencil run round the diagram in the direction of the hands of a watch, negative if in the opposite direction.

If the diagram intersect itself, some parts of its area will be positive, others negative; but the statement above applies separately to each of the parts.

352. Were this all that the diagram affords, its value (great as it is) would be mainly practical, as Watt originally designed it to be. But we must now examine it from a higher point of view.

We assume for the sake of reasoning that there is a definite amount, say unit of mass, of the working substance, and that it does not leave the cylinder; also that it has, throughout (at each instant), the same temperature and also the same hydrostatic pressure. By this last consideration our reasoning is practically restricted to fluids, whether they be liquids, vapours, or gases, or even a complex arrangement such as a liquid in the presence of its saturated vapour.

In the last of these cases there is, between the limits of volume at which the whole is liquid, or the whole is vapour, a definite relation between temperature and pressure alone. The volume, when assigned, gives us in this case the farther information *how much* of the substance is in the liquid state.

But in the first three of these cases we have seen (§§ 121, 124) that there is a definite relation between the volume, pressure, and temperature; a relation whose form depends upon the particular substance treated, but which is sufficient to determine any one of the three quantities above when the other two are assigned. That relation we assume to have been experimentally obtained for the particular substance whose behaviour we are for the time discussing.

353. But this is not all. The physical state of the substance is entirely defined when any two of these quantities are assigned. [The reader must be reminded that we are dealing with a definite quantity of the substance.] Hence, as a particular case, when the volume and pressure are assigned, the temperature can be definitely calculated. Every point, P, on the diagram thus corresponds to one temperature; and, by drawing lines, each through all the points corresponding to one particular temperature, we may cover the diagram with *Isothermals*, or *lines of equal temperature.* Portions of two of these, PP' and QQ', are roughly indicated in the diagram of section 351.

Each of these lines gives a graphic representation of the relation between the pressure and volume of the substance so long as its temperature is unchanged. This corresponds to the *second* and *fourth* of the operations in Carnot's Cycle (§ 86). The *first* and *third* operations of that cycle involve the behaviour of the working substance when it is surrounded by non-conducting bodies, and therefore cannot gain or lose heat directly. From any point in the diagram (which, as we have seen, represents a definite state of the body) we may suppose a line drawn representing the relation between pressure and volume under this new limitation. Thus the whole diagram may be covered with a new set of curves, called by Rankine *Adiabatic lines.* In the rough diagram above, PQ and $P'Q'$ represent portions of two such lines. Any other definite condition will, in general, give rise to its own particular class of lines; but the two classes we have mentioned are by far the most important for our present purpose. We must discuss their properties with some care.

354. So far, temperature may be considered as being measured on any scale, no matter how defined. But one of the great results to be developed in this chapter is the *absolute* measurement suggested to Thomson by the remarkable investigation of Carnot. Once we have got this mode of measurement, every other method must give place to it.

355. Meanwhile we make the general remark that any class of lines on the plane diagram may be regarded as successive parallel *sections* of a surface, which represents the general relation between volume, pressure, and the quantity characteristic of the class of lines. Thus the lines of equal temperature are sections, perpendicular to the axis on which temperature is measured, of the surface which gives the relation between volume, pressure, and temperature. Sections of this surface perpendicular to the axis of volumes would be a set of curves of equal volume in terms of pressure and temperature as co-ordinates. The surfaces themselves may in fact be regarded as portions of a hilly country, while the parallel sections play the part of contour lines. And all the properties of contour lines find here new and interesting applications.

Any number of such surfaces and corresponding curves of section can be devised; we will refer to those only which are of paramount importance.

356. The isothermals or lines of equal temperature might be conceived as being drawn by the indicator itself, the contents of the cylinder being kept successively at temperatures rising step by step, while at each temperature the piston is made to go to and fro in the cylinder.

We may for the moment assume these steps to be each 1° C., such as we have hitherto employed, or a definite multiple or fraction of such a degree. But one of the great objects which we have now in view is the absolute measurement of temperature. When we have secured this, we shall have an obviously appropriate rule suggested to us for drawing the successive isothermals.

357. The isothermals of the ideal perfect gas (§ 126) may be very briefly treated. Since the product of the pressure and volume is constant at any one temperature, the lines PP', QQ', in the fig. of § 351 are equilateral hyperbolas of which the lines Ov and Op are the asymptotes. These curves are all similar, and similarly situated, and the linear dimensions of each are as the square root of the corresponding absolute temperature. Thus, if drawn at successive equal intervals of temperature, they approach more and more closely to one another as the temperature is higher.

358. The isothermals of the more permanent gases, such as hydrogen, air and its constituents, &c., do not, within ordinary ranges of temperature and pressure, differ much from equilateral hyperbolas. For pressures less than about 150 atmospheres, the air isothermals lie a very little *below* the hyperbolas of the ideal perfect gas.

What happens at exceedingly small pressures is not certainly known. In fact, if the kinetic gas theory be true, a gas whose volume is immensely increased, cannot in any strict sense be said to have one definite pressure throughout. At any instant there would be here and there isolated impacts on widely different portions of the walls of the containing vessel; instead of that close and continuous bombardment which (to our coarse senses) appears as uniform and constant pressure.

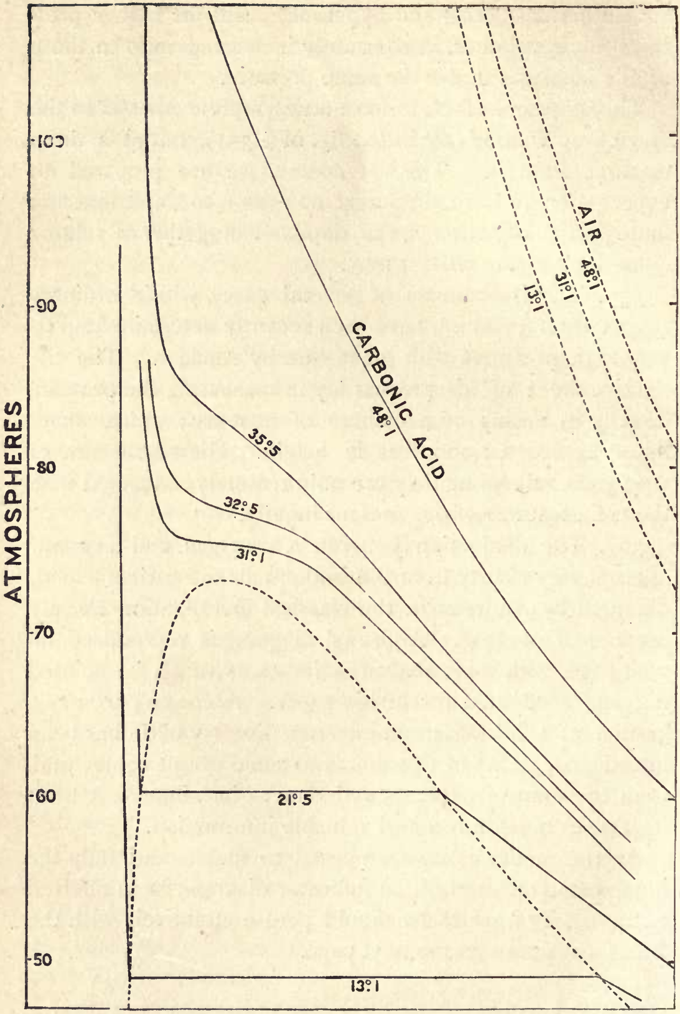
At ordinary temperatures, and about 150 atmospheres, the air isothermals cross the hyperbolas, and for higher pressures show volumes in constantly increasing ratio to those of the ideal gas under the same pressure.

They appear, in fact, to have an asymptote *parallel* to the line of no volume (*Op* in the fig. of § 351), but at a finite distance from it. This, of course, we are prepared to expect—for we have absolutely no reason to think that any finite portion of matter can be deprived altogether of volume—be the pressure what it may.

359. The isothermals of several gases, within ordinary ranges of temperature, have been recently determined up to very high pressures with great care by Amagat. The distinctive merit of his process lay in measuring the pressure directly by means of a column of mercury; which sometimes exceeded 1,000 feet in height. His results are of very great value, but they are only remotely connected with the main features of our present inquiry.

360. The distinction between a true gas and a vapour appears very clearly from the isothermals of carbonic acid, obtained by Andrews in the classical investigation already mentioned (§ 174). Andrews' diagram is reproduced on next page, with some slight modifications which he pointed out and accounted for in his paper. According to a suggestion of Clerk-Maxwell, one new line (dotted) has been introduced. Part of this line is to some extent conjectural, from the want of experimental data:—but, imperfect as it is, it gives much novel and valuable information.

As the reader is now supposed to understand fully the immediate teachings of the indicator diagram, he is referred again to § 175, which he should peruse attentively with the aid of the figure on the next page.


ATMOSPHERES
100
90
80
70
60
50
AIR
48°.1
31°.1
13°.1
CARBONIC ACID
48°.1
35°.5
32°.5
31°.1
21°.5
13°.1

This figure contains two groups of curved lines which are the isothermals for carbonic acid and air, respectively, at temperatures between 13°.1 C. and 48°.1 C.

[The masses of the two quantities of gas were not equal, so that in that respect the comparison is not of the kind which has been hitherto assumed in this chapter. For the air was used merely as a manometer, to give (by its changes of volume) the pressure of the carbonic acid at each stage of the process. The isothermals, therefore, are those of a mass of air which at 1 atmosphere and 13°.1 C. had the same volume as the carbonic acid.]

The new dotted line is drawn so as to pass through all the pairs of points on each isothermal (under the critical temperature) at which the carbonic acid either just ceases to be wholly vapour, or just becomes wholly liquid. The region included by it is therefore that *in which the vapour can be in thermal equilibrium with the liquid.* A glance at the figure shows that the limits of volume corresponding to this region gradually approach one another as the temperature is raised; the left-hand branch of the dotted curve leaning towards the right, and the right-hand branch towards the left. Thus, as the temperature is gradually raised, the smallest volume at which the carbonic acid is wholly vaporous becomes less, while the greatest volume at which it is wholly liquid becomes greater. Close to the critical temperature (but under it) these volumes are practically equal.

Also, as is obvious from the figure, the compressibility of the carbonic acid just before it is partially liquefied becomes less and less as the temperature is raised, while that of the liquid (when just completely formed) becomes greater and greater.

Thus in volume, and in compressibility, at one temperature, these two states gradually approach one another, until at and above the critical temperature they can no longer be distinguished from one another.

Thilorier's result (§ 122) as to the great expansibility of liquid carbonic acid, is obvious from the figure :—as is also its great compressibility (discovered by Andrews).

If we imagine a broken line to be drawn in the figure, formed of the left-hand branch of the dotted curve, and the critical isothermal (for the higher range of pressures) it is obvious that, for any condition represented by a point to the *left* of this line, the carbonic acid is wholly liquid. Another broken line, consisting of the right-hand branch of the dotted curve and the same portion of the critical isothermal, has to the *right* of it all points expressing conditions at which the substance is wholly non-liquid. Now, by properly applying heat and pressure, we can bring the substance by *any* path we choose (on the diagram) from one of these states to the other. Choose two such paths, one (A) wholly free of the dotted curve, the other (B) intersecting it (twice). Operate on the gas according to the B path, and we *see* it at one part of the course partly vapour and partly liquid. Return from the undoubtedly liquid state to the undoubtedly non-liquid state, by the path A. At no stage of the operation is there any indication that the substance is partly in one molecular state, partly in another.

This, however, is on the supposition, which we have hitherto made for the indicator diagram, viz., that the pressure and temperature shall be uniform at every instant throughout the whole mass of the substance operated on. If carbonic acid be in a state represented by a point near the apex of the dotted curve, very slight differences of temperature or pressure at different points of the mass give rise to extraordinary differences of optical properties ; and the whole presents, in an exaggerated form, the appearances seen when we look through a column of air ascending from a hot body, or through a vessel in which water and strong brine have been suddenly mixed.

361. The relative densities of the liquid carbonic acid and its saturated vapour are, as the diagram shows, about 5·7 : 1 at 13.°1 C. At 21.°5 C. the ratio is only about half as great. Thus there is no difficulty in representing the relative volumes graphically.

But when we deal with water and saturated steam at any ordinary temperature, the ratio of densities is (roughly) 1600 : 1. To give anything approaching this we must take carbonic acid at very low temperatures. Hence no diagram of moderate size can be constructed so as to represent fully the isothermals of water-substance, at the temperatures for which Andrews has given us those of carbonic acid. On the other hand, a diagram, somewhat resembling that of Andrews, would represent the isothermals of water for temperatures over 400° C.

362. It will be observed that in all these cases, as a rule, the isothermal lines are inclined downwards towards the right, *i.e.*, when the substance is kept at constant temperature, increase of volume implies diminution of pressure; or increase of pressure implies diminution of volume. This merely signifies that every known fluid, in whatever state it be, is compressed by the application of greater pressure, its temperature being kept unaltered.

Apparent exceptions are necessarily collapsible or explosive bodies, which suddenly and abruptly change volume when pressure is applied. Such exceptions are only apparent because in them the isothermal condition is necessarily violated.

A real exception is in the case of saturated vapour in presence of the liquid, for here the pressure remains unchanged as the volume varies, whether by diminution or by increase. This, of course, is due to the fact that part of the substance undergoes a change of molecular state, involving abrupt change of volume with considerable absorption or evolution of heat, and the proper realisation of the isothermal requires that the volume be made to alter so slowly that the change of temperature which would thus be caused can be guarded against by external applications.

363. The adiabatic lines cannot conveniently be drawn for any substance as the result of direct experiment, simply because it is impossible to make an absolutely non-conducting vessel in which to conduct the experiments. It is, however, possible to calculate their form for any class of substances by the help of theory, from the results of experiments which can be carried out. This point must be deferred for the present.

364. Meanwhile we may, but only for the purpose of reasoning (§ 86), suppose that we have the substance inclosed in a cylinder which can be made, at will, either a perfect conductor of heat or an absolute non-conductor. Let this cylinder be supposed to be surrounded by a mass of perfectly conducting liquid, whose specific heat is so great that its temperature remains practically unaltered by any transference of heat, either way, between it and the contents of the cylinder. Then, if the indicator be attached to the piston, it will trace the isothermal, or the adiabatic, according as the walls of the cylinder conduct heat or not.

365. Now suppose the substance to give out heat under compression. Let the piston be forced inwards. If the cylinder conduct, the heat developed is at once removed; but for all that the pressure in general rises, as we saw in § 362. But, if the cylinder do not conduct, the effect will be the same as if the substance, with its pressure already increased by (isothermal) compression, had farther heat

supplied to it without being permitted to change its volume. In such bodies as we are now considering, the effect will be to still further increase the pressure. Thus *the adiabatic line through any point of the diagram is more inclined to the axis of volume than is the corresponding isothermal.*

366. The same thing is true if the substance be, like water between 0° C. and 4° C., one of those which are cooled by the application of pressure, because they contract when heated. For if the cylinder be a conductor, heat passes through it into the substance, and thus the pressure becomes less than if, as in the adiabatic, heat be not allowed to enter.

The statement is still true when we are dealing with a liquid, and its saturated vapour, in presence of one another. For compression liquefies some of the vapour, and sets free its latent heat. When this is allowed to escape as it is developed, the pressure remains unchanged. But in the adiabatic the pressure must, in consequence of the heating, increase with diminution of volume.

It holds also when we are dealing with a mixture of ice and water. For here it is the ice which melts, because it is bulkier than the water produced from it, and the whole becomes colder in consequence of the latent heat required for the water which is formed. If heat be allowed to enter, so as to restore the original temperature, more ice is melted, and the pressure sinks in consequence.

367. These phenomena are instances of a general law which has been formulated independently by different physicists. Thus Helmholtz says, as to the effect of pressure on a mixture of ice and water: "Here mechanical pressure, as happens in the majority of cases of interaction of different natural forces, favours the production of the change, melting, which is favourable to the development of its own action."

Clerk-Maxwell, speaking of the greater steepness of the adiabatics than of the isothermals, says: "This is an illustration of the general principle that, when the state of a body is changed in any way by the application of force in any form, and if in one case the body is subjected to some constraint, while in another case it is free from this constraint but similarly circumstanced in all other respects, then if during the change the body takes advantage of this freedom, less force will be required to produce the change than when the body is subjected to constraint."

368. In general, any one point of the diagram corresponds to one perfectly definite state of the working substance, and therefore there can be drawn through it only one isothermal and one adiabatic The adiabatic (as we see by §§ 365, 366) *crosses* the isothermal from above downwards, and towards the right of the diagram.

But, in certain special cases, a point of the diagram may correspond to more than one essentially different state of the substance. Each of these states has its own isothermal and its own adiabatic; and thus we find it sometimes said that two or more isothermals, or adiabatics, may intersect one another.

The proper view to take of such cases is to look on them as instances in which part of the diagram *overlies* another part, so that (as in the contour lines of an overhanging cliff), though designated in the diagram by the same rectangular co-ordinates, they lie in regions which must be regarded as perfectly distinct from one another. (See, again, § 355.)

This will appear clearly enough if we consider the relation between volume and temperature in water at the ordinary atmospheric pressure. Thus (§ 121) we know that the volume of water is the same at 2° C. and at about 6° C. Hence the isothermals for water at 2° C. and at 6° C.

intersect in a point given by one atmosphere pressure and volume 1·00003. But if we think of a water thermometer, we see that the scale of such an instrument would be, as it were, *doubled back on itself*, the lowest point being at 4° C. (the maximum density point), and the scale reading upwards from this point to 5°, 6°, &c., for increase of temperature, but *also upwards* to 3°, 2°, &c., for diminution of temperature. These are not to be regarded as one scale, but as two distinct parts of a scale doubled back on itself. And in a similar way we must regard the corresponding part of the indicator diagram above mentioned.

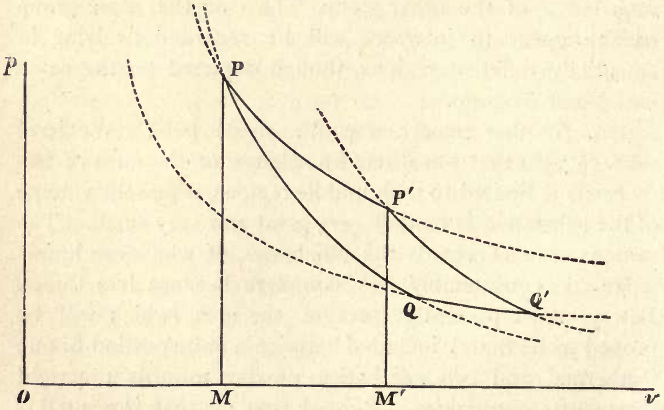
369. Hence, in the reasonings which follow, we shall consider the systems of isothermals and adiabatics as in themselves groups of non-intersecting curves; but such that each curve of one group intersects once, and once only, each curve of the other group. Two of the same group which appear to intersect will be regarded as lying in essentially different regions, though depicted on the same part of our diagram.

370. Another remark must be made here. We have seen (§ 358) that our direct knowledge of the form of isothermals is limited to their middle regions, where the volume of the substance is neither very great nor very small. The same is true as regards the adiabatics, of which our knowledge is considerably less complete because less direct. But we must presently consider the area (which will be proved to be finite), included between a finite portion of one isothermal and two adiabatics passing towards the right through its extremities. Remark that all that is wanted is a mode of completing our diagram, however imperfectly or even (as subsequent experiments may show) erroneously, provided that it can lead us into no error in the special reasoning for which it is devised, and for which *alone* it is

to be employed. Clerk-Maxwell suggests the following method which, while convenient and sufficient for our solitary object, is so obviously incorrect as to details that no one can run any risk of being misled by it.

Let *RR′R″* (in the fig. of § 374 below) be the isothermal of lowest temperature whose form we know, *QR*, *Q′R′*, *Q″R″*, . . . adiabatic lines. Draw *any line SS′S″* and call it (for our temporary purpose) the isothermal of absolute zero. Then it is clear that we may draw (each in an infinite number of different ways) lines *RS*, *R′S′*, *R″S″*, . . . such that the curvilinear areas *RR′S′S*, *R′R″S″S′* &c., shall have any assignable finite values.

371. We now recur to Carnot's *Reversible Cycle*, in order that we may be able to interpret the diagram in the light of the two Laws of Thermodynamics.



Let *PP′* be the isothermal of the working substance at the temperature t_1, of the hot body; *QQ′* that at the temperature t_0 of the cold body; while *QP* and *P′Q′* are the adiabatics of the first and third operations respectively. Also let H_1, H_0 be the quantities of heat taken in and given out respectively in the direct working of the cycle. Then, by the definition of absolute temperature (§ 95), we have

$$\frac{H_1}{t_1} = \frac{H_0}{t_0}.$$

As the cycle is reversible, no heat-transaction takes place except these, and therefore the work done is the equivalent of the excess of the heat supplied from the source over that given out to the condenser. If we choose, for convenience, to measure heat in dynamical units, we must use the word "*equal*" instead of "*equivalent*." [Joule's equivalent, as originally given (§ 37), was 772 foot lbs. for the unit of heat to the Fahrenheit degree. This is, of course, about 1,390 foot lbs. for the centigrade degree.] Hence, with this convention and the proposition of § 351, we have

$$H_1 - H_0 = \text{area } PP'Q'Q$$

372. As the extent of the isothermal expansion, P to P', may be what we choose, we will for simplicity suppose it so taken that we have numerically (the unit of heat being now the foot-pound)

$$H_1 = t_1.$$

The definition of absolute temperature then gives

$$H_0 = t_0;$$

so that, in our present system of units we have

$$t_1 - t_0 = \text{area } PP'\,Q'Q.$$

373. Now we are prepared to choose scientifically our system of isothermals and adiabatics, and thus to settle the values of the several degrees of the scale of absolute temperature.

Proceeding along the isothermal PP' in the diagram opposite, let us mark successive additional points P'', P''', &c., so that t_1 heat units are taken in from P' to P'', P'' to P''', &c., as well as from P to P'. Through the points P'', P''', &c., draw adiabatics meeting QQ' in Q'', Q''', &c. Then it is clear that the heat given out in passing from Q'' to Q', or from Q''' to Q'', &c., is (like that from Q' to Q) represented by t_0. Thus, $t_1 - t_0 =$ area $PP'Q'Q$ $=$ area $P'P''Q''Q' =$ area $P''P'''Q'''Q'' =$ &c.
And this holds whatever be the value of t_0.

Hence, if we assume t_0 to be *one degree* lower than t_1, so that $t_1 - t_0 = 1$, each of the areas $PP'Q'Q$, $P'P''Q''Q'$, &c., will be one unit. And a third isothermal, two degrees under t_1, will be one degree under t_0, and will thus cut off a new set of unit areas from the series of adiabatics.

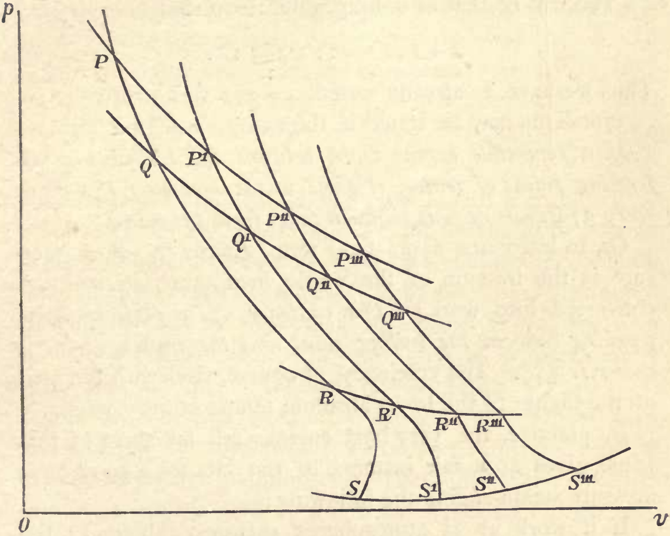
The whole explored part of the field may thus be divided into unit areas by the system of adiabatics just described, and a set of isothermals for successive degrees of temperature. But the length of a degree, so far, is perfectly arbitrary, though when its value is assigned *at any part of the scale* the whole becomes definite.

374. The area contained between two successive adiabatics of this series, and any two isothermals, has therefore as its measure the number expressed by the difference of the absolute temperatures of the isothermals.

[Here we see, at once, one of the great merits of Carnot's process. For the statement just made is altogether independent of the nature of the working substance.]

This area also represents, as we have seen, the excess of the heat supplied over that given out. Its utmost value, therefore, when the lower isothermal is that of absolute zero, is a finite quantity representing the whole heat supplied. Thus if $RR'R''R'''$. . . . be the lowest isothermal whose form is known, we may (as in § 370) take any line $SS'S''S'''$ . . . . as the isothermal of absolute zero; and the lines RS, $R'S'$, $R''S''$ &c., must be so drawn that the several areas $PP'Q'R'S'SRQ$, $P'P''Q''R''S''S'R'Q'$, ... may each be equal to t_1.

From what has been already said we see at once that whatever isothermal is represented by $QQ'Q''Q'''$, . . . the areas $QQ'R'S'SR$, $Q'Q''R''S''S'R'$, ... must also be



equal to one another. Thus the absolute temperatures in any two isothermals PP' and QQ' are to one another as the complete areas $PP'Q'R'S'SRQ$ and $QQ'R'S'SR$. The determination of the ratio of these areas, when PP' and QQ' belong to any two definite temperatures, such as those of water boiling, and of ice melting, under one atmosphere of pressure, is a matter entirely for experiment. (How such experiments have been conducted we will afterwards show.) The result for these two temperatures was found by Joule and Thomson to be nearly 1·365 : 1. (*Phil. Trans.* 1854.)

375. Hence, if we adopt the centigrade scale, but merely in so far as to divide the interval between the freezing and boiling points into 100 degrees, *whether these be the same degrees as those of our earlier scale* (§ 61) *or not;* and if x be, on our new scale, the absolute temperature of melting ice, $x+100$ will be that of boiling water:—so that

$$x+100 : x :: 1·365 : 1.$$

Thus we have, as already stated, $x=274$ very nearly.

376. This may be stated in the easily intelligible form:—*If a reversible engine work between the boiling and the freezing points of water, it gives to the condenser* 274 *out of every* 374 *units of heat which it takes from the boiler.*

Or, to introduce a practical term, *Efficiency*, whose measure is the fraction of the whole heat taken in which is converted into work:—*The efficiency of a perfect engine, working between the boiling point and the freezing point of water is* $\frac{100}{374}$. The efficiency, of course, rises with the ratio of the higher to the lower absolute temperature.

In practice, the very best engines fall far short of this. Joule gives as a fair instance of the data for a good high-pressure steam-engine the following:—

If it work at $3\frac{1}{2}$ atmospheres' pressure (about 53 lbs. weight per square inch) the temperature of the boiler must be about 300° F., and it is found practically impossible to keep the condenser at a lower temperature than about 110° F. nearly. Absolute zero on the Fahrenheit scale is $-274\frac{180}{100}+32=-461°$ F. nearly. Hence even the theoretical efficiency is only $\frac{190}{761}$, very nearly $\frac{1}{4}$. The *actual* efficiency is rarely more than about half as much.

377. To recur to our diagram, § 374. The absolute temperature, t, completely defines a particular isothermal, when we know the working substance. Let, now, ϕ be the corresponding characteristic of an adiabatic, *i.e.* the quantity which has the same value at all points of such a line. Rankine originally called it the *Thermodynamic Function*, and Clausius has since called it *Entropy*. It is obvious that ϕ depends in some way on the heat given to or taken from the substance, for it is constant only when there is no direct gain or loss of heat.

And we see at once from the equation

$$\frac{H_1}{t_1} = \frac{H_0}{t_0},$$

which is true for all values of t_1 and t_0, that the amount by which ϕ increases, in passing from one adiabatic to another along an isothermal, may be *defined* as simply the common value of these equal quantities. Thus since in our standard method of drawing a group of adiabatics (§ 372) we took H_1 numerically equal to t_1, the value of ϕ increases by unity from any one to the next of the group.

378. By working backwards through the group of adiabatics, along the isothermal t, we remove t units of heat for each unit by which ϕ diminishes. This suggests the measurement of ϕ from a zero at which the substance has no heat to part with. Practically, however, we measure ϕ (as, in dynamics, we measure a potential) from some assumed origin. For it is with its changes alone, and not with its actual value, that we are mainly concerned.

Suppose, then, that we assume for this purpose a definite point in the diagram as the origin. Draw the corresponding isothermal, say t_0, and produce it to cut the adiabatic for which ϕ is to be measured. Let the substance expand or contract adiabatically till its temperature is t_0, and let its volume then change isothermally till its state is that of the assumed origin. If H be the heat given out during this last operation, we have

$$\phi = \frac{H}{t_0}.$$

Here H may be negative, in which case ϕ is also negative.

It follows that if a substance change its state isothermally at temperature t, from ϕ_0 to ϕ, it takes in an amount of heat denoted by

$$t\,(\phi - \phi_0).$$

If it be restored to ϕ_0 along the isothermal t_0, it gives out heat to the amount

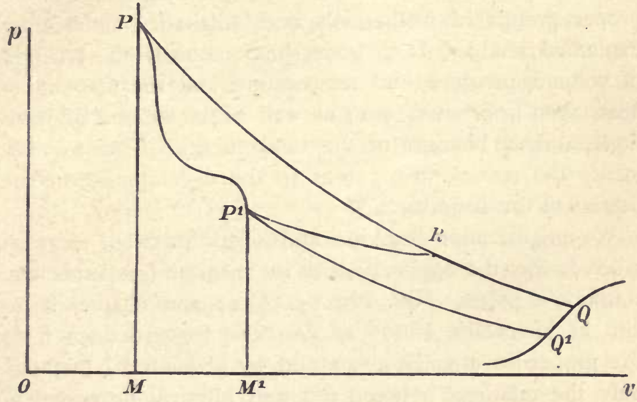
$$t_0\,(\phi - \phi_0).$$

In a Carnot's cycle, bounded by t, ϕ, t_0, ϕ_0, the excess of heat taken in over that given out, *i.e.* the work done, or the diagram area of the cycle, is thus

$$(t - t_0)\;(\phi - \phi_0).$$

379. The changes in the total energy of a substance may also be exhibited on the diagram. [The whole amount of energy in a substance is a quantity which we have no means of ascertaining. We can tell (§ 220) how much goes in, and how much comes out, and in what forms it goes in or comes out, but no more. Fortunately this is all we require for practical applications.]

Let the point P in the diagram represent the initial state of the substance, PM the line of volume, PQ the adiabatic corresponding to P. Then, if the state be altered (by any path) to one represented by a point P', there will be work done by the body, (*i.e.* loss of energy,) if P' is to the right of MP; also heat will be given out (again loss of energy) if P' lie below PQ. [We will take this as the standard case. A little consideration will show what modifications are required if P' is to the left of MP, or above PQ.] Draw the volume line $P'M'$, and the adiabatic $P'Q'$, and let QQ' be the (arbitrary) line corresponding to $S'SS''S'''$ in § 370. Then the area $PP'M'M$ is the work done, and $PQQ'P'$ the heat given out (§ 374), both represented in dynamical units. Hence the area $PQQ'P'M'M$ represents the whole loss of



energy from the state P to the state P'; and is evidently independent of the form of the path PP'.

But it is necessary to remark that each of its parts, the work done, and the heat given out, has in general a value which depends on the form of the path. This consideration is one of the utmost importance, as it enables us to represent graphically the amounts of heat which are either necessarily, or needlessly, wasted in any particular course. If, for instance, we suppose that no heat is supplied to the working substance, the course PP' cannot anywhere pass *above* PQ. Again, if P' has the lowest available temperature, PP' cannot anywhere lie *below* the isothermal $P'R$. Thus the maximum amount of work which can be obtained, in passing from one given state to the other, will correspond to expansion adiabatically along PQ, followed by compression along the isothermal to P'. In the course PP', the area $P'RQQ'$ represents the heat necessarily wasted, PRP' that wasted unnecessarily.

380. Hence we see that the improved diagram, with the proper groups of isothermals and adiabatics as recently explained, enables us to trace simultaneously the changes of volume, pressure, and temperature, and the amounts of heat taken in or given out; as well as the amount of work done, and the changes of the total energy. Thus we fully justify the remark in § 349 as to the development of the powers of the diagram.

We might, after Rankine and Clerk-Maxwell, develop much farther the applications of the diagram (see especially Rankine's paper, *Phil. Trans.*, 1854; and chaps. ix. to xiii. of Maxwell's *Theory of Heat*) so as to deduce from the properties already given, and by geometrical methods only, the relations between different physical properties of a substance. These are all ingeniously obtained by Maxwell from different expressions for the unit area of the elementary parallelogram formed by two consecutive adiabatics and two consecutive isothermals, as defined in § 373. But experience has taught us that, elegant, simple, and powerful as these methods are, they are found (by such students as are able to understand them) considerably more difficult to follow than the analytical methods.

No one who wishes thoroughly to realise Thermodynamic Theory, can safely omit the study of Clerk-Maxwell's book; but he will learn something of the subject, and be better prepared for further study, if he begins by looking at the elements of the theory from a simple analytical point of view.

381. There is, unfortunately, a wide-spread notion (of course only among those who have not taken the little trouble required to know better), that the differential calculus, even in its elements, is something terribly profound. When one of this class, as *sometimes* happens, can be persuaded to listen, he is made conscious in a very short time that many of the mental processes to which (unless he is simply an idiot) he has been accustomed since his childhood, are based on these very elements of the dreaded calculus, sometimes upon more recondite parts of it. For such people there should be no consideration, and there shall be none here.

382. *Résumé* of §§ 349–381. Watt's Indicator. Indicator Diagram. How it expresses work. Isothermal and Adiabatic Lines. Regarded as successive parallel sections of a surface. Isothermals of air, carbonic acid, water. Adiabatics steeper than isothermals. Carnot's cycle on the diagram. Absolute temperature. Efficiency of an engine. Thermodynamic Function. Entropy. Total Energy.

CHAPTER XXI.

ELEMENTS OF THERMODYNAMICS.

383. IN the preceding chapter we have exhibited, by means of the indicator diagram, many of the thermal properties of individual substances, and some of the relations which the application of the Laws of Thermodynamics has shown to exist among these. The quantities, in terms of which we there expressed the state of a substance, were at first v (the volume) and p (the pressure) of unit mass of the substance.

Then we saw that the whole explored region of the diagram could be divided into equal areas (of any size) by properly grouped isothermals and adiabatics, so that the state of the substance might equally well be expressed in terms of t (absolute temperature) and ϕ (thermodynamic function, or entropy).

But we can also easily see that we might have expressed the position of a point (*i.e.* the state of the substance) by any other pair of these four quantities :—*i.e.* in terms of v and t, v and ϕ, p and t, or p and ϕ.

And we also saw that (E) the whole energy (to a constant *près*) could be expressed in terms of p and v, and therefore in terms of any other pair of the four quantities. Hence we see that there exist three necessary relations among the five quantities

$$p, v, t, \phi, E,$$

and therefore that any three of them can be expressed in terms of the remaining two.

We proceed to develop, analytically, the more elementary results of the application of the Laws of Thermodynamics :—and we will choose sometimes one pair, sometimes another, of these five quantities (as shall best suit our immediate purpose) for the *independent variables* in terms of which the others are to be expressed.

384. We commence with the expressions for the Energy. This subject was attacked by W. Thomson in 1851.

If, under mean pressure p, the volume of the substance change from v to $v + dv$, the work done (corresponding to so much loss of energy) is

$$pdv.$$

If at the same time the substance, at mean temperature t, pass from the adiabatic ϕ to the proximate one $\phi + d\phi$, it must take in (*i.e.* gain in energy by) the amount of heat

$$td\phi$$

represented (§§ 371, 378) in dynamical units.

Thus we have, for the change of energy,

$$dE = td\phi - pdv \quad . \quad . \quad . \quad . \quad (1)$$

Hence E may be regarded as a function of the two independent variables v and ϕ, such that its partial differential coefficients are

$$\left(\frac{dE}{dv}\right) = -p, \quad \left(\frac{dE}{d\phi}\right) = t. \quad . \quad . \quad . \quad . \quad (2)$$

385. These equations tell us, respectively, that

(α) The loss of energy per unit increase of volume in adiabatic expansion is measured by the pressure.

(β) If the substance be kept at constant volume, the gain of energy, per unit increase of entropy, is measured by the absolute temperature. This is merely the same as:—At constant volume, the increase of energy is measured by the heat supplied.

386. From equations (2), by partial differentiation, we find

$$-\left(\frac{dp}{d\phi}\right) \quad \left[= \frac{d}{d\phi}\left(\frac{dE}{dv}\right) = \frac{d}{dv}\left(\frac{dE}{d\phi}\right)\right] = \left(\frac{dt}{dv}\right).$$

To interpret this equation, multiply and divide the left hand member by t, and we have:—The fall of temperature per unit increase of volume in adiabatic expansion, is equal to the increase of pressure per (dynamical) unit of heat taken in at constant volume, multiplied by the absolute temperature.

387. The expression for dE [(1) of § 384] consists of two parts, neither of which is (separately) a complete differential, though their (algebraic) sum is necessarily so. Compare § 379, where the reason is made obvious. Both the work done, and the heat supplied, depend on the form of the path (*i.e.* on the succession of states through which the substance passes) and this is wholly arbitrary. The change of energy, on the other hand, depends only on the initial and final states of the substance.

388. By adding various complete differentials to both sides of (1), we may change the independent variables to any of the other pairs v and t, p and ϕ, p and t. And from the results we can, as before, draw definite conclusions as to relations between the thermal properties of the substance.

389. Thus, for v and t as independent variables,

$$d(E - t\phi) = -\phi\,dt - p\,dv.$$

This gives, by a process precisely similar to that employed in § 386,

$$\left(\frac{dp}{dt}\right) = \left(\frac{d\phi}{dv}\right).$$

Multiplying both sides by t, this reads :—The latent heat of (isothermal) expansion is measured by the product of the absolute temperature and the increase of pressure per unit rise of temperature at constant volume.

Thus if we have steam in presence of water, or water in presence of ice (*i.e.* the same substance in two states in which the first differs thermally from the second by the latent heat, L, per unit mass) ; let v_0, v_1 be the volumes of unit mass of each at p, t ; $e : 1 - e$ the ratio in which the unit of substance operated on is made up of these forms,

$$v = ev_0 + (1 - e)\,v_1.$$

Hence

$$\left(\frac{dp}{dt}\right) = \frac{1}{v_0 - v_1}\left(\frac{d\phi}{de}\right).$$

The first member is the rate at which pressure must change with temperature so that there shall be no change of volume, *i.e.* no alteration of the relative proportions of the parts of the substance in the two different states.

The second, multiplied by t, is the heat which must be supplied per unit increase of volume, the temperature remaining unchanged. Hence $L\,de$, the latent heat required for the change of state represented by de, must be equal to $t\,d\phi$, the heat supplied.

Thus the preceding equation takes the form

$$\left(\frac{dp}{dt}\right) = \frac{L}{t\,(v_0 - v_1)}.$$

For small simultaneous changes of pressure and temperature, this becomes

$$\delta t = \frac{t(v_0 - v_1)}{L}\delta p,$$

since under the assigned conditions, p is a function of t only, not of v (§§ 362, 366).

Thus, when $v_0 > v_1$ (as with steam and water), the temperature is raised by increase of pressure: but when $v_0 < v_1$ (as with water and ice), the temperature of the mixture falls when the pressure is raised.

As a test let us consider the dimensions (§ 345) of the above expression. Term for term they are

$$[\Theta] = \frac{[\Theta][\mathrm{L}^3]}{[\mathrm{FL}]}\left[\frac{\mathrm{F}}{\mathrm{L}^2}\right]$$

390. The formula above is equivalent to that given by J. Thomson in 1849 (§ 142) from Carnot's principle alone. Let us deduce a numerical result. A cubic foot of water at 0° C. weighs about 62·5 pounds. Hence the volume of a pound of water is about 0·016 cubic feet. The density of ice is (§ 145) 0·92, so that the volume of a pound of ice is [$0{\cdot}016 \div 0{\cdot}92 =$] 0·0174 cubic feet. The latent heat of water is (§ 151) 79·25 units of heat, which must be multiplied by Joule's equivalent, 1390 (§ 371), to reduce it to foot-pounds. One atmosphere of pressure is about 2117 pounds weight per square foot. Hence, calculating from the formula, we find that the freezing point is lowered by

$$0^\circ{\cdot}0074 \text{ C.}$$

for each atmosphere of pressure.

391. We cannot *directly* apply this process to a numerical calculation in the case of water and steam, for experimental difficulties of a formidable character lie in the way of the

determination of the density of saturated steam at different temperatures. Still, if we take the corresponding values of δp and δt from Regnault's table (§ 164), and L from § 166, we may use the formula to calculate the volume of one pound of saturated steam at any temperature.

But a curious result, due to Rankine and Clausius, may easily be deduced. Let c_0, c_1 (functions of t alone) be the specific heats of any substance in its two states of saturated vapour, and liquid, in the same vessel. Then remembering that the condition of unit mass of the substance is fully characterised by the quantities t and e, we have for the heat required to change these to $t + dt$, and $e + de$, respectively,

$$t d\phi = (c_0 e + c_1 (1 - e))\, dt + L\, de \quad . \quad . \quad . \quad . \ (1).$$

Hence $$\frac{d^2\phi}{dt\, de} = \frac{d}{de}\left(\frac{c_0 e + c_1 (1 - e)}{t}\right) = \frac{d}{dt}\left(\frac{L}{t}\right);$$

or, $$c_0 - c_1 = \frac{dL}{dt} - \frac{L}{t}.$$

Now by § 166, dL/dt for steam is (roughly) $-0·7$; so that as $c_1 = 1$ for water, $dL/dt + c_1 = 0·3$. But L/t has the values 2·2, 1·4, 0·98 at 0°, 100°, and 200° C. respectively. Hence, we find that c_0 is negative.

To investigate the results of adiabatic compression on steam in the presence of water, note that (§ 393) the mixture is heated, so that dt does not vanish, but has a positive value. Now the left-hand member of (1) is zero. Hence in order that de may vanish, *i.e.* that there may be neither evaporation nor liquefaction, we must have

$$(c_1 - c_0)\, e = c_1.$$

[Since c_0 is negative, the value of e is a proper fraction.]

If the steam be in excess of this ratio, the value of de is positive, so that compression leads to further evaporation; if in defect, some steam is liquefied. (See, again, § 86.)

Saturated steam, when no water is present, becomes superheated by adiabatic compression.

Also, if saturated steam is allowed to expand in a vessel impervious to heat, it cools so as to keep at the temperature of saturation; and, besides, a portion of it liquefies.

This result appears at first sight inconsistent with the paradoxical experiment long known, that high-pressure steam escaping into the air through a small orifice does not scald the hand, or even the face, of a person exposed to it; while, on the contrary, low-pressure steam inflicts fearful burns. W. Thomson has explained the difficulty thus:—The steam rushing through the orifice produces mechanical effect, immediately wasted in fluid friction, and consequently *reconverted into heat*, from which, by Regnault's numerical data, it follows that the issuing steam (in the case of the high-pressure, but not of the low-pressure, boiler) must be over 100° C. in temperature, and *dry*.

392. Again we have from our fundamental equation,

$$d(E + pv) = td\phi + vdp,$$

whence, as before,

$$\left(\frac{dt}{dp}\right) = \left(\frac{dv}{d\phi}\right).$$

Introducing t as a divisor of each side, we read:—The rate of increase of volume, per unit of heat supplied at constant pressure, is the ratio of the adiabatic rate of change of temperature with pressure to the absolute temperature.

393. Finally

$$d(E - t\phi + pv) = -\phi dt + vdp,$$

whence

$$-\left(\frac{d\phi}{dp}\right) = \left(\frac{dv}{dt}\right).$$

Introducing t as a factor on both sides, we have:—The heat given out per unit increase of pressure at constant temperature is equal to the product of the absolute temperature by the rate of change of volume per unit rise of temperature at constant pressure, *i.e.* to the continued product of the absolute temperature, the volume, and the expansibility.

Thus we see that bodies which expand by heating are heated by compression, while those which contract by heating (as water under its maximum density point) are cooled by compression.

394. We have seen (§ 121) that, for temperatures near to the maximum density point, we have for water

$$\frac{1}{v}\frac{dv}{dt} = \frac{t-278}{72{,}000}.$$

Hence, for one additional atmosphere of pressure, the heat developed in unit mass of water (about this region of temperature) is, in dynamical units (see § 390),

$$\frac{2117\,t(t-278)}{62\cdot5 \times 72{,}000};$$

and it therefore produces a rise of temperature

$$\frac{2117}{62\cdot5 \times 1390} \cdot \frac{t(t-278)}{72{,}000} = \frac{t(t-278)}{2{,}950{,}000}$$

nearly. Thus the change of temperature produced, in water at 0° C., by a sudden increase of pressure to the amount of 150 atmospheres (roughly 1 mile of sea water, or a ton weight per square inch), would seem to be about

$$-0^\circ\cdot055 \text{ C.}$$

This result, however, is considerably too large, because we have not taken account of the fact that the maximum density point is notably lowered by so large a pressure as 150 atm., and in consequence the expansibility of water at 0° C. is correspondingly diminished. To take account of this, let

$$\epsilon = \frac{1}{v}\left(\frac{dv}{dt}\right) \text{ and } \kappa = -\frac{1}{v}\left(\frac{dv}{dp}\right)$$

represent respectively the expansibility and the compressibility; p and t being the independent variables. We see at once that

$$\left(\frac{d\epsilon}{dp}\right) = -\left(\frac{d\kappa}{dt}\right),$$

or:—The rate at which the expansibility of a substance is raised by increase of pressure is equal to the rate at which its compressibility is diminished by rise of temperature. Thus Canton's early result (§ 121) shows that water, at ordinary temperatures, becomes more expansible (or, as the case may be, *less contractile*) under pressure.

Now the relation between small simultaneous changes of pressure and temperature which leave the expansibility unchanged is given by

$$0 = \delta\epsilon = \left(\frac{d\epsilon}{dt}\right)\delta t + \left(\frac{d\epsilon}{dp}\right)\delta p.$$

By means of the above relation we see that this may be put in the form

$$0 = \left(\frac{d\epsilon}{dt}\right)\delta t - \left(\frac{d\kappa}{dt}\right)\delta p.$$

But experiment gives, at ordinary temperatures and pressures, the approximate expression

$$\kappa = 0{\cdot}000052 - 0{\cdot}0000003\,\tau,$$

where τ is temperature C. Hence, as the maximum density point is subject to the present conditions, being that of zero expansibility, it is lowered through

$$0^\circ{\cdot}02$$

by one additional atmosphere.

We may now write the more accurate expression for the expansibility at ordinary temperatures

$$\frac{1}{v}\frac{dv}{dt} = \frac{t - 278 + 0{\cdot}02\,p}{72{,}000}$$

and we find that the change of temperature produced by 150 atmospheres in water at 0° C. is only

$$-\frac{150 \times 274(4 - 150 \times 0{\cdot}01)}{2{,}950{,}000} = -\,0^\circ{\cdot}035\text{ C},$$

or about two-thirds of the former estimate.

In the case of water at 8° C., the effect of 150 atmospheres is to raise the temperature about one-thirteenth of a degree.

395. If k be the specific heat of a substance at constant pressure, we have for the unit mass

$$k\,dt = t\,d\phi$$

with the condition

$$dp = 0.$$

If we choose, as is usually done, v and t as independent variables, these equations may be written

$$k\,dt = t\frac{d\phi}{dt}dt + t\frac{d\phi}{dv}dv$$

$$0 = \frac{dp}{dt}dt + \frac{dp}{dv}dv.$$

Now $t\dfrac{d\phi}{dt}$ is obviously the specific heat at constant volume, c, suppose. For it is the rate at which heat is supplied per degree of rise of temperature, when the volume of unit mass of a substance is kept constant. Hence these equations give, by elimination of the special ratio of dt to dv enforced by our condition,

$$k - c = -t\frac{d\phi}{dv}\frac{\dfrac{dp}{dt}}{\dfrac{dp}{dv}} = -t\frac{\left(\dfrac{dp}{dt}\right)^2}{\dfrac{dp}{dv}},$$

which (since by § 362, $\dfrac{dp}{dv}$ is negative) is obviously always positive. This applies to all substances in which there can be uniform hydrostatic pressure, but it takes an exceedingly simple form for the ideal perfect gas.

396. The thermodynamic relations of the ideal perfect gas may next be taken, as they are all excessively simple and form at least fair approximations (within ordinary ranges of temperature and pressure) to those of gases or gaseous mixtures such as hydrogen, oxygen, air, &c.

Here (§ 126) our fundamental condition is

$$pv = Rt.$$

To find the form of the adiabatics, we have (§ 389)

$$\frac{d\phi}{dv} = \frac{dp}{dt} = \frac{R}{v}.$$

We have also

$$\frac{dp}{dv} = -\frac{p}{v},$$

so that (§ 395)

$$k - c = +t\left(\frac{R}{v}\right)^2\frac{v}{p} = R.$$

Hence, as

$$t\frac{d\phi}{dt} = c,$$

we have

$$d\phi = \frac{c}{t}dt + \frac{k-c}{v}dv$$

$$= \frac{c}{p}dp + \frac{k}{v}dv.$$

Thus

$$pv^{k/c} = C\epsilon^{\phi/c}$$

gives, for various assigned values of ϕ, the form of the adiabatics for the ideal perfect gas.

397. As Laplace first pointed out, the compressions and dilatations of air, in the passage of sound, take place so rapidly that there is no time for much more than a tendency towards equalisation of temperature, and the changes of volume therefore take place adiabatically.

Thus we have, as the relation between pressure and volume during the passage of sound, the relation

$$pv^{k/c} = \text{constant},$$

instead of

$$pv = \text{constant},$$

i.e. Boyle's Law, which was employed by Newton for the solution of this most important problem.

The ordinary process for the investigation of the motion of plane waves (which would be out of place here), gives for the velocity of sound, with the above relations between pressure and volume, the respective expressions

$$\sqrt{\frac{k}{c}Rt} \qquad \text{(Laplace).}$$

$$\sqrt{Rt} \qquad \text{(Newton).}$$

R and t, as well as the velocity of sound, can be directly measured; and thus from Laplace's result the ratio k/c can be determined with considerable accuracy. (See, again, § 187.)

Rankine was the first to give a theoretical determination of the specific heats of air, which rivalled in accuracy the subsequent experimental determinations of Joule and Regnault. His method was founded on this value of the ratio of k to c, combined with the value of the difference $k - c$, as calculated from the formula of § 395.

398. To discover how ordinary gases deviate in their behaviour from the ideal perfect gas, many methods have been employed, of which that devised by Thomson (as an improvement of one of Joule's methods) is the most interesting and instructive in its consequences. We will first describe Joule's experiment of 1844, already referred to, and then consider Thomson's improvement of it.

Temperature C. on the air-thermometer bears, by definition, the same ratio to 100° that the expansion of air at constant pressure [or the increase of pressure at constant volume], from the freezing-point to that temperature, bears to the corresponding expansion [or increase of pressure] from the freezing-point to the boiling-point.

399. By his experiment, presently to be described, Joule proved that, to a considerable degree of accuracy, the heat developed in the compression of air is the equivalent of the work spent.

This is a truth, but not a truism. And the following words of Clerk-Maxwell, whether or not they shall ever come to be carefully considered by the reckless partisans at whom they were aimed, are at least calculated to convey a much needed and salutary lesson:—

" This is by no means a self-evident proposition. In fact, it is not true in the case of substances which are not in the gaseous state, and even in the case of the more imperfect gases it deviates from the truth. Hence the calculation of the dynamical equivalent of heat, which Mayer founded on this proposition, at a time when its truth had not been experimentally proved, cannot be regarded as legitimate."

British science has not as yet been so warmly cherished by British statesmen that it can afford to have some of its very best achievements wrongly attributed to foreigners.

400. Joule took a strong vessel containing compressed air, and connected it with another equal vessel which was exhausted of air. These two vessels were immersed each in a tank of water. After the water in the tanks had been stirred carefully, so as to bring everything to a perfectly uniform state of temperature, a stop-cock in the pipe connecting the two vessels was suddenly opened. The compressed air immediately began to rush violently into the empty vessel, and continued to do so till the pressure became the same in both ; and the result was, as every one might have expected, that the vessel from which the air had been forcibly extruded fell in temperature in consequence of that operation. It had expended some of its energy in forcing the air into the other vessel. But that air, being violently forced into the other vessel, impinged against the sides of that vessel, and thus the energy with which it was forced in through the tap was again converted into heat. Thus the air which was forced into the vacuum became hotter than before, while the air which was left behind became colder than before. But, on stirring the water round these vessels, after the transmission of air had been completed, and the stop-cock closed, Joule found that the number of units of heat lost by the vessel and the water on the one side was almost precisely equal to the quantity of heat which had been gained on the other side.

He then repeated the experiment, employing instead of two tanks of water, each holding one of the two strong vessels, one larger tank also filled with water, with both vessels buried side by side in it: then, on allowing part of the air to escape, as before, from the one into the other, and stirring till everything had acquired exactly a common temperature, he found that there was scarcely any measurable change in temperature.

These experimental methods proved indisputably that the quantity of heat lost by the one part of the air was:—at least as nearly as so rough an experiment enabled him to test it:—equal to the quantity of heat gained by the other.

401. Now the compressed air had at first a certain capability of doing work. It might have been used to drive a compressed-air engine for instance; but in its final state, when it had expanded to double its original bulk, it had not so much available working power stored up in it as it had before. There was, therefore, dissipation of part of the energy, originally present; and yet the apparatus and its contents had not lost any heat.

There was, on the whole, no heat lost, because what was lost to the one vessel was gained by the other. No heat was given out to external bodies, and no available work was done. The air was simply allowed to expand—to change its bulk—without driving out pistons or doing anything by which it could convey work to external bodies. It had, therefore, at last precisely the same amount of energy as at first; and yet of that not nearly so much was available. The air had seized at once the chance given it of dissipating part of its energy, and did dissipate it, as far as was compatible with the circumstances of the arrangement.

402. The really curious point about this is, that in order to restore the lost availability to the energy of the air—to get the air back into its former condition, so as to be capable of doing as much work as it was capable of doing at first—it would be necessary to spend work upon it, pumping half of it back from the second vessel into the first; but the amount of work which would be spent in pumping it back goes to heat the whole mass of air; and, when work enough to force back the air into the first vessel from the second has been expended, the amount of heat which is given out during the process—which can be measured with great exactness—is almost precisely equivalent to the work which is spent in forcing the air back.

Thus, to restore to the energy its former availability, no supply of energy is required, but some high-class energy must be degraded. Work has been spent, and we have got instead its less useful heat-equivalent. We must waste a certain amount of energy, or rather get a lower form of energy in place of it, in order to restore to the mass of air the availability of the energy which it possessed originally, and which it had been allowed to lose during its sudden expansion.

403. Thomson's modification of this experiment resembles in some respects the process of Regnault described in § 186. The gas to be experimented on is made to pass, as uniformly and noiselessly as possible, through a tube in which there is an obstruction, in the form of a porous plug, such as a pellet of cotton-wool or the like. The temperature of the stream is carefully measured on each side of the plug, and at such distances from the plug as to avoid the local irregularities produced by it.

Since the motion is uniform, equal *masses* of the gas pass in equal times through the various cross sections of the tube.

Let the pressures before and after passing the plug be p and p', the corresponding volumes of unit mass v and v'.

Then pv is the work done on unit mass of the gas as it passes a cross section of the tube before reaching the plug, while $p'v'$ is the work it gives out as it passes a section after leaving the plug. Their difference is the gain of energy, provided no heat be supplied from without, and no energy lost as sound. Hence, since the motion is regarded as uniform, if E and E' be the intrinsic energy of unit mass before and after passing the plug,

$$E' - E = p\,v - p'v',$$

or the conditions of the experiment are such that

$$E + p\,v$$

is constant.

Therefore (§ 392),

$$t\delta\phi + v\delta p = 0,$$

or, taking p and t as independent variables,

$$t\frac{d\phi}{dt}\delta t + t\frac{d\phi}{dp}\,\delta p + v\delta p = 0.$$

Now $t\dfrac{d\phi}{dt}$ is here evidently the specific heat at constant pressure, which (§ 395) we called k. Also (§ 393) we have

$$\frac{d\phi}{dp} = -\frac{dv}{dt} = -ve$$

if e be the expansibility at constant pressure. With these values our equation becomes

$$k\delta t = -v(1 - et)\,\delta p \quad . \; . \; . \; . \quad (1)$$

Here t represents absolute temperature. To compare this with the scale of a gas-thermometer, let T be the temperature Centigrade on such a thermometer, corresponding to the absolute temperature t; the lengths of the degrees on the two being assumed as equal throughout the (very small) range of the experiment. Then we have, by § 124,

$$pv = C(1 + aT)$$

as an approximate expression, to be rectified. Thus, as the degrees are practically equal on the two scales, throughout the small range of change,

$$e = \frac{1}{v}\frac{dv}{dT} = \frac{a}{1 + aT}$$

and therefore

$$k\delta t = -v\left(1 - \frac{at}{1 + aT}\right)\delta p,$$

$$= -C\Big(1 - a(t - T)\Big)\frac{\delta p}{p} \quad . \; . \; . \; . \; (2)$$

Thus, finally,

$$t = T + \frac{1}{a} + \frac{k\delta t}{R\frac{\delta p}{p}}$$

In the experiments of Joule and Thomson, the changes of pressure and temperature are not infinitesimal. To adapt the formula to such a case we may lawfully integrate (2), through the small range of the experiment, neglecting the variation of $t - T$. Thus if the observed change of temperature be θ, and the pressures p and p', the formula becomes.

$$t = T + \frac{1}{a} - \frac{k\theta}{R(\log. p - \log. p')}.$$

404. The first two terms of this expression give the result of § 126, directly suggested by Charles' Law. The third term was found by experiment to be small for bodies at temperatures above their critical points, *i.e.* for true

gases; and considerably larger for vapours. All the true gases, except hydrogen, were slightly colder after than before passing the plug; hydrogen slightly warmer. It was by these experiments that the temperature of absolute zero was determined (§ 374) to be very nearly − 273°·7 on the Centigrade scale.

405. The following little table exhibits the main features of Joule's and Thomson's results, so far as the air-thermometer is concerned. The numbers in the first column (each with 273°·7 added) are absolute temperatures. Those in the second column are the quantities to be added to the corresponding absolute temperatures to give temperatures by the air-thermometer, when the air is kept at the density corresponding to 0° C. and 1 atmosphere of pressure. The third column gives the corresponding numbers for the air-thermometer when the pressure is maintained throughout at one atmosphere. (*Phil. Trans.* 1854.)

DIFFERENCE BETWEEN AIR-THERMOMETERS AND ABSOLUTE SCALE.

Absolute Scale.	Constant Volume.	Constant Pressure.
273°·7 + 0	+ 0·	+ 0·
+ 20	+ 0·0298	+ 0·0404
+ 40	+ 0·0403	+ 0·0477
+ 60	+ 0·0366	+ 0·0467
+ 80	+ 0·0223	+ 0·0277
+ 100	+ 0·0000	+ 0·0000
+ 120	− 0·0284	− 0·0339
+ 140	− 0·0615	− 0·0721
+ 160	− 0·0983	− 0·1134
+ 180	− 0·1382	− 0·1571
+ 200	− 0·1798	− 0·2018
+ 220	− 0·2232	− 0·2478
+ 240	− 0·2663	− 0·2932
+ 260	− 0·3141	− 0·3420
+ 280	− 0·3610	− 0·3897
+ 300	− 0·4085	− 0·4377

406. Joule's earliest determinations of the value of the dynamical equivalent of heat were made by working a porous plug or piston up and down in a cylinder full of water, and measuring the change of temperature produced for a given difference of pressure above and below the plug. Equation (1) of section 403 gives us the means of making the necessary calculation. For δt is measured; δp is known; v is the volume of water present multiplied by the number of up and down strokes made by the piston; and the remaining quantities, e and t, may be estimated with sufficient accuracy by the air-thermometer. The result is k in dynamical units; *i.e.* the value of Joule's equivalent itself, because the value of k in thermal units is simply unity.

407. In §§ 78-81 a first notion was given as to the dissipation of energy. Closely connected with this is the *Restoration* of energy, a question also first treated by W. Thomson. The tendency of heat (whether by conduction, radiation, or convection) towards equalisation of temperature, *i.e.* to loss of *availability*, gave the first hint of dissipation or degradation. It becomes, then, an interesting problem to seek what amount of work can be obtained, by perfect engines, from an assigned distribution of heat.

408. If we continue to measure heat in dynamical units, the dynamical value of the quantity H is simply H itself, whatever be the temperature of the body which contains it. But the utmost realisable value, unless we have a body at absolute zero to act as the condenser of a perfect engine, is always less. In fact, if t be the absolute temperature of the hot body, and t_0 the lowest available temperature of the condenser, the realisable value is (§ 376) only

$$\frac{t - t_0}{t} H,$$

or,
$$H - t_0 \frac{H}{t}.$$

Suppose that we operate upon a number of bodies at different temperatures; some being used to supply heat, others to have heat supplied to them; then the work will be simply

$$\Sigma\,(H),$$

the excess of the heat taken from some of the bodies over that given to others. This must always, except when perfect engines are employed, be *less* than the realisable value

$$\Sigma\,(H) - t_0\,\Sigma\left(\frac{H}{t}\right).$$

Hence we see that the expression

$$t_0\,\Sigma\left(\frac{H}{t}\right)$$

is necessarily *negative;* except when perfect engines only are used, *in which case alone its value is zero.* This is Thomson's expression for the heat dissipated during the cycle of operations.[1]

We have already shown, in § 379, how to treat such a question when the operations are not cyclical. The representation in symbols presents no difficulty.

409. When this mode of investigation is applied to any distribution of heat in a body, or system of bodies, it leads to the measurement of the available energy, or, as W. Thomson proposes to call it, the *Thermodynamic Motivity* of the system. This is "the possession, the waste of which is called dissipation."

410. Motivity may be regarded from without, or from within the system.

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[1] See *Phil. Mag.* May 1879.

In the former case it is the utmost amount of work which can be obtained from the system by reducing the temperatures of all its parts to some assigned temperature; —suppose that of an infinite medium by which the system is surrounded.

In the latter case it is the utmost amount of work which can be obtained by equalising the temperatures of the various parts of the system among themselves.

In either case the expression for its value has the form

$$\Sigma\, m \int_{t_0}^{t} c\frac{t - t_0}{t}\, dt,$$

where m is any element of mass, c its specific heat in dynamical units, t its absolute temperature, and t_0 the final temperature to which the whole system is to be reduced.

For $mcdt$ is an element of heat, in a body at temperature t. Of this, the amount $mc\,\frac{t - t_0}{t}\,dt$ can be realised by a perfect engine with condenser at t_0. The integration sums up all the heat thus realised till m is cooled to t_0. And the sign Σ collects these quantities for the separate masses of the system.

When the system is regarded from without, t_0 is given; and the value of this expression can be calculated at once.

When the system is regarded from within, t_0 must be determined by the condition that if a new body at that temperature had been used as a condenser for the engines using the heat of the hotter parts of the body, and as a source to which the colder parts of the body acted as condensers, it should on the whole have neither gained nor lost heat. This condition is expressed by

$$\Sigma\, m \int^{t} c\frac{t_0}{t}\, dt = 0.$$

[For, when the temperature, t, of one of the masses is higher than t_0, the quantity H leaving that mass *deposits* $\frac{t_0 H}{t}$ in the body at t_0. But when t is lower than t_0, the supply of H to the mass at t necessitates the *taking* of $\frac{t_0 H}{t}$ from the body at t_0. The *form* of the expression is therefore the same in either case; and the distinction between giving and taking is provided for by the fixed order of the limits in the integral, which is taken from a lower to a higher temperature in the former case, and from a higher to a lower in the latter.]

From this t_0 can be calculated, and the expression for the motivity then takes the very simple form

$$\Sigma\, m \int_{t_0}^{t} c\,dt.$$

411. One very curious consequence of this is, that if the system consist of two equal masses, m, of the same substance, at temperatures t_1 and t_2, and if we assume the specific heat to be independent of the temperature, the common temperature when the internal motivity has been entirely realised is

$$\sqrt{t_1\, t_2},$$

and the motivity itself is

$$m\,c\,(\sqrt{t_1} - \sqrt{t_2})^2.$$

Thus the internal motivity of a system consisting of a pound of ice-cold water and a pound of boiling water is, in foot-pounds,

$$1390\,(19{\cdot}339 - 16{\cdot}553)^2 = 1390 \times 7{\cdot}76.$$

The absolute temperature to which the system is reduced, when its internal motivity is thus exhausted, is

320·12, corresponding to 46°·12 C.

But, if the two parts of the system had been simply mixed, the resulting temperature would have been 324, or 50° C. Hence the energy would have been greater by that of 2 lbs. of water raised 3°·88, *i.e.* by the quantity of work 1390 × 7·76 obtained in the former process. But this excess of energy is only in part available. With an unlimited external system at temperature 46°·12 C. we can realise only about

1390 × 0·048 foot-pounds.

Thus when the water is, in each case, brought to the uniform temperature of 46°·12 C., we realise more than 160 times as much work by the first process as by the second.

412. The entropy of a system changes along with its motivity; but the two things are quite distinct, as the following simple case shows.

When the element, H, of heat is in a body at temperature t_1, its motivity is (as we have seen)

$$\frac{t_1 - t_0}{t_1} H,$$

where t_0 is the lowest available temperature. Hence, if this heat be transferred to another body at a lower temperature t_2, the *loss* of motivity is

$$\left(\frac{t_1 - t_0}{t_1} - \frac{t_2 - t_0}{t_2}\right) H = t_0 \left(\frac{1}{t_2} - \frac{1}{t_1}\right) H.$$

On the other hand, when the element H of heat passes from a body at temperature t_1, to another at temperature t_2, the first body loses entropy to the amount $\frac{H}{t_1}$, and the second gains to the amount $\frac{H}{t_2}$ (§ 378); so that the whole entropy of the system *increases* by the amount

$$\left(\frac{1}{t_2} - \frac{1}{t_1}\right)H.$$

Thus the *loss* of motivity is simultaneous with *gain* of entropy. But the loss of motivity by the passage of heat from a warmer to a colder body is less as the lowest available temperature is lower; while the corresponding gain of entropy is the same whatever be this lowest temperature.

413. The only effect of a limit of temperature, on the entropy, is to limit its final amount. But if the external universe were at the temperature of absolute zero, there need be (theoretically) no loss of motivity, *i.e.* no dissipation of thermal energy; while the entropy would go on increasing without limit as the heat gradually passed to colder bodies.

Thus we see that Clausius' theorem, "*The entropy of the universe tends to a maximum*," is by no means identical with, though it is closely connected with, Thomson's previously published theory of dissipation.

414. In § 195 we promised to give Thomson's investigation of the phenomena of the Thermo-electric circuit. We can now do so, by the help of the formulæ of this chapter.

Let t_0, t be the absolute temperatures of the junctions in a circuit of two metals, in which the specific heat of electricity has the values σ_1, σ_2 respectively. Let T be the temperature of the neutral point, and Π the Peltier effect of unit current passing through the junction at temperature t. Then the change of E, the electromotive force, caused by raising the temperature of the hot junction from t to $t+\delta t$, will be

$$\delta E = \frac{d\Pi}{dt}\delta t + (\sigma_1 - \sigma_2)\,\delta t,$$

for it must be remembered that the direction from hot to cold is necessarily reversed in passing from one to the other of the two metals.

But the change of the expression

$$\Sigma\left(\frac{H}{t}\right)$$

which (§ 408) is always zero for a set of reversible operations, such as this is (§ 195) supposed to be, gives

$$\frac{d}{dt}\left(\frac{\Pi}{t}\right)\delta t + \frac{\sigma_1 - \sigma_2}{t}\delta t = 0.$$

Without any assumption as to the expression for $\sigma_1 - \sigma_2$, we may eliminate it from these equations, and we obtain the very interesting result

$$\frac{dE}{dt} = \frac{\Pi}{t}.$$

[Hence we see at once that Π vanishes at the neutral point, for then (§ 193) E is a maximum, and therefore

$$\frac{dE}{dt} = 0.]$$

This equation shows that the value of Π may be completely determined from measurements of the current in the circuit as depending on the temperature of the hotter junction, the colder being kept at constant temperature. Conversely the comparison of the observed currents with corresponding measures of the Peltier effect, would enable us to test the admissibility of the assumptions we have made.

415. So far, we have been following Thomson. But if we now introduce the experimental result (§ 197) that the specific heat of electricity is proportional to the absolute temperature, we have

$$\sigma_1 = k_1 t, \qquad \sigma_2 = k_2 t,$$

and our equations become

$$\frac{dE}{dt} = \frac{d\Pi}{dt} + (k_1 - k_2)t,$$

$$\frac{d}{dt}\left(\frac{\Pi}{t}\right) + (k_1 - k_2) = 0.$$

The second gives

$$\frac{\Pi}{t} = C - (k_1 - k_2)t,$$

$$= (k_1 - k_2)(T - t).$$

because Π vanishes at the neutral point.

With this, the first gives finally

$$E = (k_1 - k_2)(t - t_0)\left(T - \frac{t + t_0}{2}\right).$$

Thus we see that the expression for the electromotive force has no other variable factors than the two; the first of which was of course known to Seebeck, while the second was discovered experimentally by Thomson.

The constant factor, $(k_1 - k_2)$, is the same in the expression for the E.M.F., and in that for the Peltier effect. Hence we cannot, by measuring either of these quantities, find more than the algebraic *difference* between the specific heats of electricity in the two metals.

The measurement of the actual amount of the Thomson effect in some one metal must therefore be carried out directly.

All the results of this section are, however, quite easily obtained by mere inspection of the diagram (§ 196).

A general notion of the first effect produced by an electric current on the distribution of temperature in a wire will be found in *Nature*, xxxiv. 121.

416. *Résumé* of §§ 383, 415. The state of unit mass of the working substance can be expressed in terms of any two of the five quantities, energy, volume, pressure, temperature, and entropy. Hence various thermodynamic relations among these. Relation between specific heats. Development of heat by compression. Determination of absolute temperatures in terms of air-thermometer. Restoration of energy. Thermodynamic motivity. Comparison with entropy. Theory of the thermoelectric circuit.

CHAPTER XXII.

NATURE OF HEAT.

417. EVERY ONE has heard of the celebrated phrase "*Ohne Phosphor, kein Gedanke.*" Be what there may of truth in this, the facts stated in the preceding chapters entitle us to say "*Without motion, no heat.*" But just as from the first statement, even if it were proved to be absolutely true, we should not be entitled to say that "Thought is phosphorus":—so the second by no means implies that "Heat is motion." It is therefore much to be regretted that some of the highest modern authorities on the subject, such as Clerk-Maxwell and Sir W. Thomson, have occasionally been betrayed into the use of this phrase in the form in which it was originally employed by Rumford and Davy, before clear ideas had been obtained about energy; and that they have thus given an unintentional support to a practice altogether inconsistent alike with their usual mode of speaking of heat, and with their knowledge of its true nature. For, in their less unguarded statements, such men invariably speak of heat as energy. The word *Motion* has two different uses; the one, popular as well as scientific, referring to mere change of position:—the other, purely scientific, meaning (after Newton) momentum. It is, of course, in the former of these senses that the word is used

with regard to heat:—for its use in the latter sense would not be merely slipshod, it would be untrue. In the posthumous MSS. of Sadi Carnot, published for the first time in 1878, we find that he carefully guards himself in his statements on this matter. Thus he says:—Un mouvement (celui de la chaleur rayonnante) pourrait-il produire un corps (le calorique)? Non, sans doute, il ne peut produire qu'un mouvement. *La chaleur est donc le résultat d'un mouvement.* Alors il est tout simple qu'elle puisse se produire par la consommation de puissance motrice, et qu'elle peut produire cette puissance. [This is one of the very striking passages to which we referred in § 84 above.]

418. Heat, like all other forms of energy, can be perceived by us only while it is being transformed or transferred. We cannot individualise any portion of it so as to be able to recognise it again, any more than we can distinguish, in a vessel of water, the portions of the contents which were put in first from those which were afterwards added. As we have already seen (§ 220) we can tell how much heat enters a body, and how much leaves it; what it is *in the body* is quite another question. That some of it, at least, is in the form of kinetic energy we know from the facts of radiation. For we have seen that all bodies radiate, *i.e.* communicate vibratory energy to the luminiferous medium. This can only be in consequence of motions of the particles of the body, for it is not motion of the body as a whole. And we have seen that radiation is not confined to the surface of a body. Hence all the particles (by which, for the moment, we mean literally "little parts," parts too small to be distinguished by the microscope) of a hot body must be in motion. But there are two quite distinct kinds of motion which these particles may have:—motion of each particle *as a whole*, relative to the others, and motion of the

parts of a particle relative to its centre of inertia. This consideration, as we shall see later, leads to some very important consequences.

419. How much of the energy in a body is that of invisible motions of its small parts is, for the majority of bodies, still an extremely obscure question.

Before entering on a short discussion of the subject, it is necessary that we should briefly consider what is known as to the ultimate structure of matter. This leads, of course, to a considerable digression.

420. That even apparently homogeneous liquid or solid matter, such as a mass of water, of glass, or of gold, though in our most powerful miscroscopes it still preserves the appearance of homogeneity, has ultimately a certain *coarse-grainedness* or heterogeneity, is made certain by a great variety of facts. Thus, as water is a compound body, it is quite clear that the division of a drop of it cannot, even in thought, be carried farther than a certain limit, if the parts are still to be portions of *water*. This, it must be remarked, is absolutely independent of the question between *atoms* and the infinite divisibility of matter. The only mode of escape from the conclusion would be to suppose the doctrine of *Impenetrability* untrue:—*i.e.* to suppose that the same (indefinitely small) portion of space could be simultaneously occupied by hydrogen and by oxygen. Such a form of argument, however, is too metaphysical to be admitted into physics.

421. Fortunately, we can dispense with it. Heterogeneity of ultimate structure is *proved* by (1) the difference of the refractive indices of every substance for light of different wave-lengths; (2) the phenomena of contact electricity; (3) the behaviour of liquid films, as in a soap-bubble; and (4) the behaviour of gases. To the last of

these, as more intimately connected with our subject than the others, we must here confine ourselves. The results of the kinetic theory will be given, and compared one by one with the known properties of gases.

422. The atomic speculations of the old Greek philososophers, which have been so lucidly expounded by Lucretius, have always more or less affected more recent thought; and probably had a share in suggesting to Hooke and Bernoulli (§ 39) their notion of the cause of pressure in a gas. That notion was revived by Lesage and Prevost; and again in this country by Herapath, in a very curious work:—but the first precise calculations based on it were made by Joule. He showed that, if the pressure of a mass of hydrogen be due to the continual impacts of its particles on the walls of the containing vessel, the speed (assumed to be the same for all the particles) must be about 6055 feet per second, at 0° C., and 1 atmosphere pressure. Also that, the volume being supposed to remain constant, this speed increases in proportion to the square root of the pressure. These calculations were of a very simple character, as they took no account of the number or size of the particles, or of their mutual impacts. [The more complete investigations which have since been made have shown that this result is correct if, for the supposed uniform speed of the particles, we substitute the (so-called) velocity of *mean square.*]

423. We may easily see how Boyle's Law can be arrived at by this elementary hypothesis. For, suppose a gas to be inclosed in a cylinder, and suppose that we could, *without altering the common speed of its particles*, compress it into half its former bulk by pushing in one end of the cylinder. Then the number of impacts, per second, on the ends of the cylinder would be doubled; because the lengths of the paths of the particles from end to end have been

reduced to half, while the speed of the particles remains the same. Also the impacts on the curved sides of the cylinder are just as numerous and as intense as before, but they are applied to only half as great a surface. Thus the pressure is everywhere doubled.

Joule's calculation, referred to above, may be made as follows. Let M be the whole mass of the gas in a cube whose side is l, u the speed of each particle, n the number of particles. Then, if we suppose one-third of them to be moving perpendicular to each pair of faces, the number of impacts per second made by any one particle on any one face is $u/2l$. Hence the whole number of impacts per second on a face is $nu/6l$. Also each impact *reverses* the speed of a mass M/n, so that its measure is $2Mu/n$. And the pressure per unit surface of the face is found by multiplying the value of each impact by their number, and dividing by the area of the face. It is therefore $Mu^2/3l^3$, or one-third of the product of the density of the gas by the square of the common speed of its particles. Thus we may write, as the result of this approximate investigation,

$$pv = \tfrac{1}{3} Mu^2,$$

and the Law of Boyle and Charles at once suggests that the absolute temperature is proportional to the whole kinetic energy of the particles.

424. An easy extension shows how to estimate the specific heats, if we assume that the whole kinetic energy of the particles is increased by the energy of the heat communicated. But here Clausius found it necessary to take into account the *internal* energy of each particle, whether due to rotation or to relative motion of its parts. If we assume that this bears on the average a constant ratio to its energy of translation, we find that the experimental facts of this part of the subject can be accounted for.

425. The words put in italics in section 423 merit special remarks, which can only in part be made as yet:—so we must recur to them. In pushing down the piston work is done against the pressure of the gas, and we know that the result is that the gas is heated, and (§ 365) that its pressure increases adiabatically, *i.e.* more rapidly than according to Boyle's Law. To prevent this, the heat due to compression must be removed as it is communicated. Thus work is spent, and its equivalent in heat communicated to the surroundings of the cylinder. In other words, there is dissipation of energy. But if the italicised statement could be realised in practice, there would be restoration of energy without any expenditure of work. For the motivity of the compressed gas would be increased, without any expenditure of work; though the energy of motion of its particles would not be altered.

426. It is to Clausius that we are indebted for the earliest approach to an adequate treatment of this question. He was the first to take into account the collisions between the particles, and to show that these did not alter the previously obtained results. He has also the great credit of introducing the statistical methods of the theory of probabilities, and of thus giving at least approximate ideas as to the probable length of the *mean free path*, *i.e.* the average distance travelled over by a particle before it impinges on another, and thus has its course changed. He thus explained also the slowness of diffusion of gases, and their very small conductivity for heat. Clerk-Maxwell shortly afterwards improved the theory by introducing, also from the statistical point of view, the consideration of the variety of speeds at which the different particles are moving; Clausius having expressly limited his investigations by assuming for simplicity that all moved with equal speed. Maxwell explained gaseous friction, and gave a more

definite determination of the length of the mean free path.

These investigators, with the able concurrence of Boltzmann and others, have since still farther extended the theory. All that we can attempt here is to give a general account of their more prominent results. This will be done, as far as possible, in such a way as to show how far the theory is capable of accounting for known facts :—for it is by this, and this alone, that the validity and adequacy of a theory can be judged. Our plan forbids the introduction of the more complex mathematical processes, so that we can (as a rule) merely give the assumptions, with their chief theoretical consequences. But we must make an exception in favour of a method which has practically superseded those previously employed in the treatment of this question.

427. Assuming that the gaseous contents of a vessel consist of independent particles which exert certain forces on one another, while the average distribution of the particles, and of energy among them, is subject only to slight and very rapid periodic changes, Clausius in 1870 established a perfectly general theorem which is symbolically expressed as follows :—

$$\tfrac{1}{2}\Sigma(mu^2) = \tfrac{3}{2}pv + \tfrac{1}{2}\Sigma(Rr).$$

Here the left-hand side is the whole kinetic energy of the system, half the sum of the products of each mass m, by the square of its speed u. If the parts of a particle move relatively to the centre of inertia of the whole, the kinetic energy of this motion must be included. The right-hand side consists of two terms, the first of which is a mere numerical multiple of the product of the volume and the pressure on the containing walls (supposed uniform). The second term, which Clausius names *Virial*, depends on the mutual action between pairs of particles (which is assumed to be exerted in the direction of the line joining them). Each element of it is the product of this force R (positive when there is attraction) into the distance r between the two particles. In this term must be included the part due to distance between portions of the same particle.

428. If we suppose for a moment that the particles are small hard bodies, exerting no action on one another except when they are in collision, the term

$$\Sigma (Rr)$$

depends merely upon the impulses, multiplied by the common diameter of the particles.

When the diameter is small in comparison with the average distance of any particle from its nearest neighbours (*i.e.* when the whole space occupied by the particles is small in comparison with the volume of the gas) this term is negligible :—so that the equation practically reduces itself to the form

$$\tfrac{1}{3}\Sigma (mu^2) = pv.$$

This is, in a slightly different form, the relation given by Joule (§ 423); and, as already stated, it leads us (by comparison with the Law of Boyle and Charles) to regard the absolute temperature of a gas in this condition as directly proportional to the kinetic energy.

When the particles are assumed to be equal, smooth, hard spheres, whose diameters are comparable with the average distance between contiguous ones, the equation is found to take the approximate form

$$\tfrac{1}{3}\Sigma (mu^2) . \left(1 + \frac{\beta}{v}\right) = pv,$$

where β is four-fold the sum of the volumes of the particles. For a given total kinetic energy (*i.e.* for an isothermal) the gas now shows greater resistance to compression than before, and this effect increases rapidly as the volume is diminished. The equation just written shows a fair agreement with the behaviour of hydrogen, from ordinary temperatures upwards.

But the deviations, from the Law of Boyle and Charles, which are exhibited under ordinary circumstances of pressure and temperature by the more easily liquifiable gases (and by the so-called permanent gases at temperatures sufficiently low, and pressures sufficiently high) are to be accounted for by molecular attraction between the particles. In this case the virial equation takes some such form as

$$\tfrac{1}{3}\Sigma(mu^2)\,.\left(1+\frac{\beta}{v}\right)=pv+\frac{A}{v+a},$$

where A/v^2 is approximately the molecular pressure of Laplace. This shows at once how, for a given amount of kinetic energy, the molecular force tends to increase the compressibility of the gas:—or, what comes to the same thing, to reduce its resistance to compression.

The first on the whole soundly-based suggestion of an equation of this species, viz.

$$\tfrac{1}{3}\Sigma(mu^2)=\left(p+\frac{a}{v^2}\right)(v-b),$$

is due to Van der Waals; who seems to have been led to it by endeavouring to extract from the virial the part due to Laplace's molecular pressure. Though objections may be freely taken to this particular equation, as well as to parts of the process by which it was obtained, there can be no doubt that the mere suggestion of it formed an extremely important step towards the solution of this very interesting and difficult problem.

But so soon as we introduce the idea of a molecular action between the particles of a gas, and the consequent increase of kinetic energy which they acquire in merely approaching one another, we are brought face to face with a new and excessively serious difficulty:—viz. What *now* represents the absolute temperature of the group of particles? Until this point is settled, we cannot put the virial equation into the desired form of a relation among p, v, and t, which is to take the place of the Laws of Boyle and Charles. Van der Waals and Clausius assume that the whole kinetic energy is still proportional to the absolute temperature. Clerk-Maxwell is more guarded:—for he says "we have no evidence that any other law holds for gases, even near their liquefying point"; while Sir W. Thomson and others have gone at least so far as to express doubt on the subject. The question cannot be even provisionally answered, at least with any feeling of confidence, until we have the solution of the purely dynamical problem:—Find the ultimate average distribution of kinetic energy in two systems of impinging particles, which are separated from one another by a flexible, inextensible, massless diaphragm; when one of the systems, only, has molecular forces among its particles.

Further remarks on this subject are thus, for the present at all events, unsuited for an elementary treatise:—and it happens, fortunately, that the great majority of the results now to be given were obtained without the introduction of molecular forces:—so that the temperature difficulty was either not raised, or raised only in an indirect manner.

429. Clerk-Maxwell showed that if there be a mixture of two kinds of particles, they will interchange energy until the average kinetic energy is the same for each species of particle. Hence it follows that when masses of different gases are at the same temperature and pressure *the number of particles per unit volume is the same in each*. This is what chemists call Avogadro's Law (also pointed out by Ampère in 1814).

He also demonstrated that, in a mixture of gases in hydrostatic equilibrium under the action of gravity, each gas behaves as if the others were absent. Further, that in equilibrium, under gravity alone, conduction would lead to uniform temperature throughout a gaseous column. [From this, by a simple application of Carnot's process, we show at once that gravity can have no influence on the thermal equilibrium of any substance.]

430. A remarkable relation, deduced from the kinetic theory, enables us to approximate to the length of the mean free path of the particles of a gas. For this is shown to bear, to the diameter of any one particle, the same ratio as the volume of the gas bears to about $8\frac{1}{2}$ times the whole bulk of the particles. If we assume that, in the liquid state, the particles are very nearly in contact, we can find approximately the size of a particle from the relative densities of the gas and the liquid. Thus it is found that the number of particles of gas in a cubic inch, at ordinary temperature and pressure, is somewhere about 3×10^{20}; while if it be oxygen, the mean free path is about $\frac{1}{450000}$ inch, and the velocity of mean square about 1550 feet per second. It follows that, on the average, each particle has about 7,600 million collisions with others per second.

431. Now we are prepared to understand why it is that the oxygen and nitrogen of our atmosphere are so thoroughly mixed that all analyses of different portions of the same mass of air give exactly the same ratio of the oxygen to the nitrogen. If each cubic inch contained only a dozen or two of particles, the theory of probabilities shows that in a large extent of air there would be, at any instant, certain cubic inches in which the relative proportions of the constituents might be any whatever. Even then this state of things could last only for an exceedingly small fraction of a second. But, in consequence of the enormous number of

the particles in each cubic inch, the probability of one single cubic inch of the lower atmosphere being (even for a moment) exclusively filled with oxygen or nitrogen alone, becomes practically a vanishing quantity. Spaces less than the trillionth part of a cubic inch will, however, occasionally (but only for periods less than the billionth part of a second) contain oxygen or nitrogen particles alone. [These numbers are purposely stated in the roughest terms, but they give all that we require :—a notion of the relative magnitudes involved.]

432. The following experiment, due to Graham, is one of the most beautiful and suggestive in the whole range of physical science :—while it requires, for its successful performance, no training whatever.

Take a hollow ball of unglazed clay, and lute into its neck a glass tube of moderate bore, so as to form a vessel resembling a large thermometer. Invert it, full of air, and plunge the open end of the tube into water. The difference of levels of the water inside and out settles in a short time into that due to capillary forces, and there remains. [Had the ball been made of glazed clay, or of glass, the water inside would not have risen so high :—in fact, by pushing the tube farther down we should obtain a permanent depression of the level of the inner surface.] This state of things is maintained by the absolute equality of the numbers of particles continually passing opposite ways through the fine pores of the clay. Unfortunately we cannot mark the particles, so as to be able to see directly that the contents of the apparatus are steadily changing. We must use another method. If we could arrange matters so that the number passing in should be greater than those passing out, gas would bubble out from the end of the tube :—if fewer entered than escaped, atmospheric pressure would cause the water to rise in the tube. Now this is precisely what happens when an atmosphere of coal-gas (collected in an inverted beaker) is made to surround the ball. The moment it is applied, air begins to bubble rapidly out from the tube. If this be continued for a little, till the contents of the bulb are mainly coal-gas, the moment the beaker is removed the water rapidly rushes up: showing in either case how much more rapidly coal-gas passes through the pores than does air.

The rates of passage of different gases under similar conditions are inversely as the square-roots of their densities.

But the main purpose for which we have described the experiment here is to show how thoroughly independent of one another are the particles of a gas, and how fast they must be moving, even at ordinary temperatures; and thus to give an additional and very strong argument in favour of the kinetic theory.

Here, incidentally, we have a first method of testing the equality of the various particles of any one gaseous substance. For a gas consisting of particles of different sizes would be partially *sifted* (as it were), by allowing half of it to diffuse through the clay ball. Half of the remainder may then be allowed to diffuse, and so on. It is clear that we should thus have a process somewhat analogous to what the chemists call *Levigation;* and by repeating it sufficiently often, we might obtain two specimens of the same gas of different densities (at the same temperature and pressure).

433. Additional, and equally strong, arguments in favour of the theory are furnished by the diffusion of one gas into another, without the use of a porous septum as in the experiment above described. The general laws of this diffusion are found to be precisely such as are indicated by the theory; and the careful measures of Loschmidt have

enabled us to arrive at much more definite ideas of the actual size and number of the particles in various gases than could be obtained by the rough assumption indicated in § 430 above. The following approximate numbers are taken from Clerk-Maxwell's (1873) Bradford Lecture on *Molecules*:—

	Hydrogen.	Oxygen.	Carbonic Oxide.	Carbonic Acid.
Velocity of mean-square at 0° C.	6190	1550	1656	1320
Mean path	386	224	193	151
Collisions	17750	7646	9489	9720
Diameter	2·3	3	3·5	3·7

The collisions are here given (as in § 430) in millions per second; the mean path and the diameter in hundred millionths of an inch; and the speed in feet per second.

434. Another valuable confirmation of the theory is afforded by the satisfactory manner in which it accounts for what would otherwise be an extremely puzzling fact—the existence of viscosity in gases. This, however, is at once seen to be a consequence of inter-diffusion between layers of gas moving with different velocities, and thus, as it were, sliding over one another. For this process obviously tends to do away with the relative velocity of the two layers, and thus produces precisely the same kind of effect as the ordinary friction between solids.

435. The conduction of heat in a gas is obviously to be attributed to the transference of energy by impacts of the more quickly moving particles on the others. The kinetic theory gives very simple relations among the numerical coefficients of diffusion, viscosity, and heat-conduction in a gas. But these could not easily be made intelligible without a more careful examination of the theory than our limits permit. Nor can we do more than point out that it has also been successfully applied to the explanation of the

processes of evaporation and dissociation, which (as we have seen in § 231) have a considerable resemblance to one another. In the one case we have a particle of the liquid moving so fast that it tears itself away from the rest in spite of the molecular forces. In the other case a compound particle is struck so sharply by another that its constituents are separated in spite of their chemical affinity.

436. We saw in § 418 that, besides the motions of the particles of a gas as wholes, there are generally relative motions of the different parts of a particle. *These* motions are at least in part communicated to the luminiferous medium in the form of transverse vibrations, and probably account for the main loss of energy in the radiant form. Of this, however, we cannot be absolutely certain, for we are altogether ignorant of the mode in which energy is transferred from ordinary matter to the luminiferous medium :—and it is possible that there may be a direct transfer even when the particle is moving merely as a whole. In such a case there would be something producing effects similar to those of a resisting medium; but in what form the energy thus transferred would be stored or propagated in the luminiferous medium we have no knowledge.

437. So long as a particle is pursuing its free path, we should expect its internal motions to be of perfectly definite periodic character, like those of a bell for instance. Hence, if the particles are all equal and similar, we are prepared to find that rarefied gases, when their temperature is sufficiently raised, give out one or more radiations each of perfectly definite wave-length. This corresponds to one or more bright lines in the spectrum. But even with absolutely equal particles these lines cannot be perfectly sharp; for, though all the particles are vibrating in precisely the same periods, some are approaching the spectator, and others

receding from him, with velocities not negligible in comparison with that of light. Hence, from this cause, which tells more as the temperature is higher, the lines are of finite (though small) breadth. At the instants of collision, the vibrating body is under constraint, and the periods are necessarily altered. The result of this action also tends in the direction of broadening the lines, but it is practically insensible when the gas is very rare; unless it be in extremely great thicknesses, for then (as we saw in § 305) it behaves as a black body.

But the effect of compression, the temperature being supposed to be maintained unaltered, is to reduce the time during which a particle is free from collisions: — *i.e.* to make the constrained radiation a larger fraction of the whole. And this effect steadily increases with farther compression, the lines gradually broadening out until we have a practically continuous spectrum. Such is necessarily the case when the body is in the liquid or the solid state.

438. Another point of importance, in which also experiment has fully verified the previsions of theory, is that the more sharp the impact the greater will be the number of vibrations of shorter periods called into play; as well as the greater the intensity of the lower forms. Hence the spectral lines increase in intensity as the temperature rises, and new ones of higher refrangibility come into view. But we must not pursue this discussion, as we have not, in the preceding pages, entered with any detail into the methods and results of spectrum analysis. (See *Nature*, xxiv. 582.)

439. There remains, however, one point of fundamental importance on which our present subject enables us to obtain more light:—the nature of the evidence for the *Second Law of Thermodynamics* (§ 82). The proof which we gave in passing, in § 93, rests entirely on the assumption

(which is essentially that of W. Thomson) that we cannot convert into work heat derived wholly from the colder of the two bodies employed in the process. If we look on this statement in the light of the definition in § 410, it will be seen to amount to this:—that it is impossible to obtain work by a process which at the same time increases the intrinsic motivity of the system we employ.

Clausius, who was the first to state Carnot's principle in a manner consistent with the true theory of heat, offered in support of it merely the following argument, with which he concludes a statement analogous to that of § 93:—"This contradicts the general deportment of heat, which everywhere exhibits the tendency to annul differences of temperature, and therefore to pass from a *warmer* body to a *colder* one."

As will be seen presently, heat does pass (though on an almost infinitesimal scale) from colder to hotter bodies. And a thermo-electric current, from a sufficient pile of elements, can raise a fine wire to a higher temperature than that of any of the junctions.

Several years later, Clausius put his argument into the following form:—"Heat cannot, of itself, pass from a colder to a warmer body." The words "of itself" he afterwards interpreted into "without compensation." This form is not liable to the thermo-electric objection above. Clausius' basis thus ultimately becomes, "In all uncompensated transformations there is increase of entropy."

440. The true basis of the second law is to be found in the extreme number and minuteness of the particles of matter:—and the consequent impossibility of dealing with them individually. For, by mere frictionless constraint, we can transfer energy of translatory motion from one body to another; so that, if we could operate on each particle

of a gas separately, we might transfer at least the greater part of their motion to one and the same body; and thus the motivity of the system might be notably increased without any external application of work.

441. If, in the illustration of § 423, we suppose the piston to move in, bit by bit, those parts only advancing upon which (for the moment) there is no impact, the consequences there mentioned would be realised :—no work would be spent, the energy of the gas would remain unaltered, but its motivity would be increased. The multitude and minuteness of the particles of the gas render this impossible; and thus we are forced to conclude that, to increase the motivity of the gas, without increasing its energy, we must *degrade* a portion of energy by applying it as work to compress the gas, and then removing its equivalent in the form of heat.

And in fact, as the statement of § 431 shows, heat does of itself pass from colder to hotter bodies. For the same argument which applies to the relative amounts of two different gases at different parts of a mixture applies also to the relative amounts of slow and fast moving particles of any one gas. But this, of course, is only on the same exceedingly minute scale as in the former case.

442. Clerk-Maxwell has treated the question from this point of view with great clearness. He says :—

"One of the best-established facts in thermodynamics is that it is impossible in a system inclosed in an envelope which permits neither change of volume nor passage of heat, and in which both the temperature and the pressure are everywhere the same, to produce any inequality of temperature or of pressure without the expenditure of work. This is the second law of thermodynamics, and it is undoubtedly true as long as we can deal with bodies only in mass, and have no power of procuring or handling the separate molecules of which they are made up. But if we conceive a being whose faculties are so sharpened that he can follow every molecule in its course, such a being, whose attributes are still as essentially finite as our own, would be able to do what is at present impossible to us. For we have seen that the molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform, though the mean velocity of any great number of them, arbitrarily selected, is almost exactly uniform. Now let us suppose that such a vessel is divided into two portions, *A* and *B*, by a division in which there is a small hole, and that a being, who can see the individual molecules, opens and closes this hole, so as to allow only the swifter molecules to pass from *A* to *B*, and only the slower ones from *B* to *A*. He will thus, without expenditure of work, raise the temperature of *B* and lower that of *A*, in contradiction to the second law of thermodynamics.

"This is only one of the instances in which conclusions, which we have drawn from our experience of bodies consisting of an immense number of molecules, may be found not to be applicable to the more delicate observations and experiments which we may suppose made by one who can perceive and handle the individual molecules which we deal with only in large masses."

443. It is to be hoped that, in time, the mathematical treatment of this statistical (not dynamical) problem may be brought within the range of students in general. This appears to be quite possible, though no attempt of any value seems yet to have been recorded.

But the real difficulty of the whole theory (beside, of course, the tremendous one of temperature, § 428) and one which, even when overcome, will probably be capable of treatment only by methods far beyond the grasp of the ordinary reader, is that (so far as it has yet been developed) it has not been reconciled with the observed values of the specific heats of gases in general. To account for the large number of lines in the spectrum of a glowing gas, it is necessary to assume that the constituents of each particle have a great many *degrees of freedom*, *i.e.* of perfectly distinct kinds of relative motion. But, at least in the present mode of applying the theory, every additional complexity of the gaseous particle seems to require that the ratio of its intrinsic energy to its energy of translation shall be made larger. Thus the calculated values of the specific heats are as a rule much too large. But it would appear that the difficulty has been unnecessarily increased by the assumption that, on the average, the whole energy is shared in *equal* proportions by each degree of freedom. This is not likely, so far at least as the *character* of the radiation of a gas at different temperatures can afford us any information on the subject. But such outstanding difficulties, grave as they certainly are, must not prevent our acceptance of a theory alike elegant and simple, and one which has already explained in an unexceptionable manner a whole series of apparently unconnected facts. (See, again, § 438.)

444. In the present state of science we are not likely to take the course of Clairaut, D'Alembert, and others who, when they found the calculated motion of the moon's nodes to differ considerably from that given by observation, proposed to modify the gravitation law of the inverse square of the distance, in spite of the almost innumerable series of facts which had been exactly accounted for by means of it:—forgetting altogether that, in forcing the law to suit the results of their calculations of this special phenomenon, they were thereby rendering it totally unfit for the purposes to which it had already so fully adapted itself.

445. It is mainly the existence of difficulties like those above referred to, which are felt throughout every portion of the now extensive range of physical science, that gives such a zest to the struggles of its true votaries. If science were all reduced to a matter of certainty, it could be embodied in one gigantic encyclopædia, and too many of its parts would then have for such men little more than the comparatively tranquil or, rather, languid interest which we feel in looking up in a good gazetteer such places as Bangkok, Ak-Hissar, or Tortuga. A science which could be completed would have far less interest than a dead language; it would sink to the level of a puzzle of which we had discovered the key.

But we have merely to think of the ideas which we try to express by such words as Time, Space, and Matter, to see that, however far discovery may be pushed, our little "clearing" can never form more than an infinitesimal fraction of the "boundless prairie." No part of this, however, can strictly be called inaccessible to unaided human reason, if time and patience fail not. But far beyond in one sense, though in another sense ever intimately present with us, are the higher mysteries of the true Metaphysic, of which our senses and our reason, unaided, are alike unable to gain us any information.

446. *Résumé* of §§ 417–445. Nature of heat in a body. Grained structure of matter. Kinetic gas theory. Calculation of speed of hydrogen particles. Statistical methods. Virial. Relation of Kinetic Energy to Absolute Temperature. Law of Avogadro. Mean free path. Number of collisions. Transpiration of gases. Viscosity, diffusion, thermal conduction. Real basis of Second Law. Present difficulties of the kinetic theory.

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